SEPTEMBER 1959 • VOL. 15, NO. 9

THE SOCIETY OF

# PLASTICS ENGINEERS JOURNAL

EDITORIAL DEPT.
UNIVERSITY MICROFILMS, INC.
313 N. FIRST ST.
ANN ARBOR, MICH.

## 1ST NATEC LOS ANGELES

PLASTICS IN AIRCRAFT AND MISSILES
NEW MOLDING MATERIALS
REINFORCED PLASTICS

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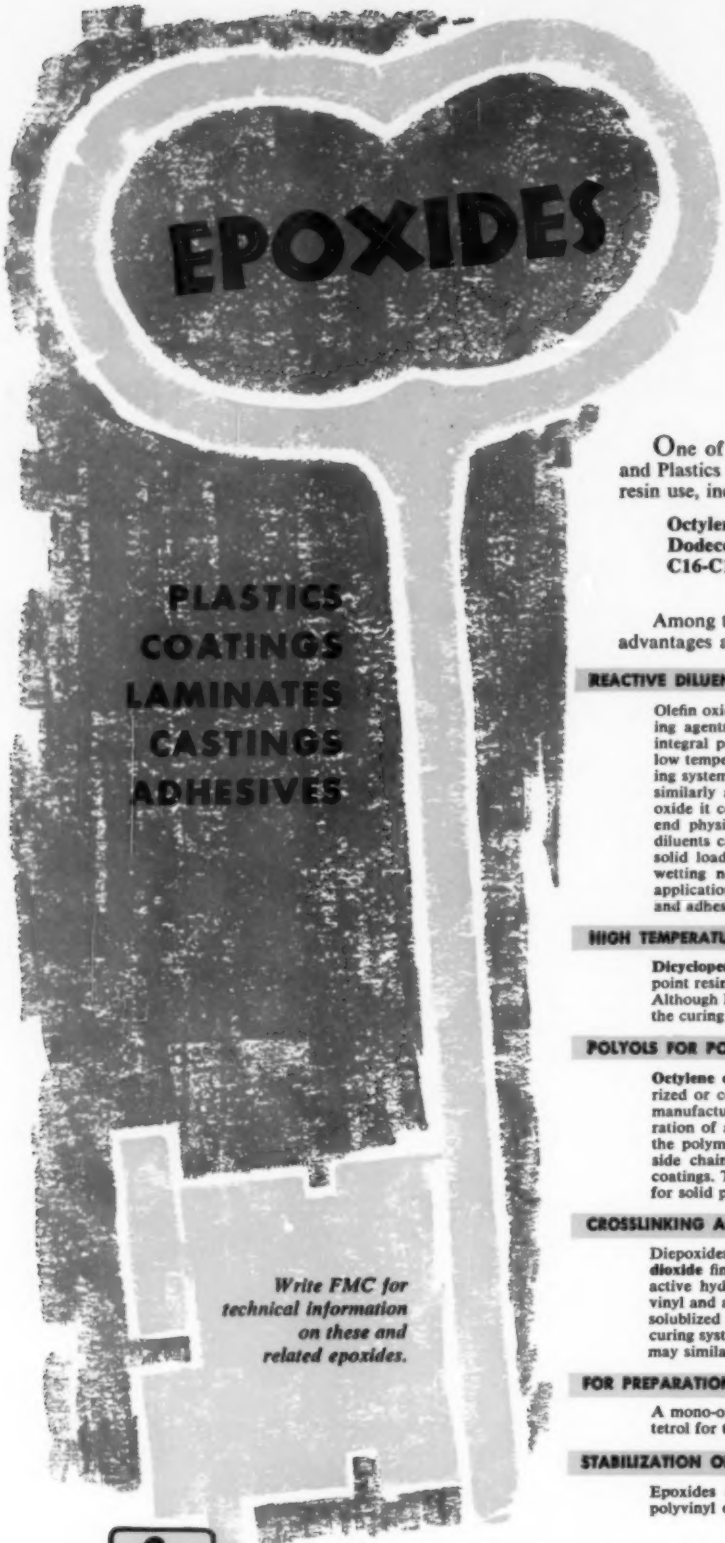


# ...the key to improved resin formulations

One of the major suppliers of epoxides, FMC Chemicals and Plastics Division offers a broad range of these chemicals for resin use, including:

**Octylene Oxide**
**Dodecene Oxide**
**C16-C18 Olefin Oxide**
**Limonene Monoxide**
**Alpha-Pinene Oxide**
**Limonene Dioxide**
**Dicyclopentadiene Dioxide**

Among the areas where these epoxides contribute significant advantages are:

### REACTIVE DILUENTS AND MODIFIERS FOR EPOXY RESINS

Olefin oxides such as **Octylene oxide** are efficient viscosity reducing agents, entering into the curing reaction and becoming an integral part of the final resin. Auxiliary benefits are improved low temperature flexibility, prolonged pot life for polyamine curing systems, and moderated exotherm. **Limonene dioxide** can be similarly applied as a reactive diluent. As a bifunctional diepoxide it contributes viscosity reduction with minimum effect on end physical properties, such as heat distortion point. These diluents can be used in casting applications particularly at high solid loadings, and in preparation of laminates where efficient wetting necessitates a low viscosity material. They also have application as reactive solvents for 100% active coating systems and adhesives.

### HIGH TEMPERATURE RESINS

**Dicyclopentadiene dioxide** gives extremely high heat distortion point resins on curing with anhydrides in the presence of glycols. Although **Dicyclopentadiene dioxide** is itself a high melting solid the curing formulations are liquid and have good pot life.

### POLYOLS FOR POLYURETHANE RESINS

**Octylene oxide** and related olefin oxides can be homo-polymerized or copolymerized to give unique polyols for polyurethane manufacture. Use of small amounts of **Octylene oxide** for preparation of a propylene oxide polyol breaks up the crystalinity of the polymer and contributes to improved flexibility. The alkyl side chains contribute to improved solubility of polyurethane coatings. The high carbon-hydrogen to oxygen ratio is of interest for solid propellants based upon polyurethanes.

### CROSSLINKING AGENTS

Diepoxides such as **Dicyclopentadiene dioxide** and **Limonene dioxide** find use as crosslinking agents for polymers containing active hydrogen functional groups, e.g. carboxy, amino. Thus, vinyl and acrylic polymers containing carboxy groups may be insolublized and crosslinked after being laid down with a dioxide curing system. Curable liquid resins with active functional groups may similarly be crosslinked as in casting applications.

### FOR PREPARATION OF ALKYDS AND POLYESTERS

A mono-oxide may be considered as a diol and a diepoxide as a tetrol for the preparation of modified alkyds and polyesters.

### STABILIZATION OF CHLORINATED RESINS

Epoxides are excellent stabilizers for chlorinated polymers as polyvinyl chloride, chlorinated rubbers, etc.

*Write FMC for technical information on these and related epoxides.*

*Putting Ideas to Work*

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**Chemicals and Plastics Division**
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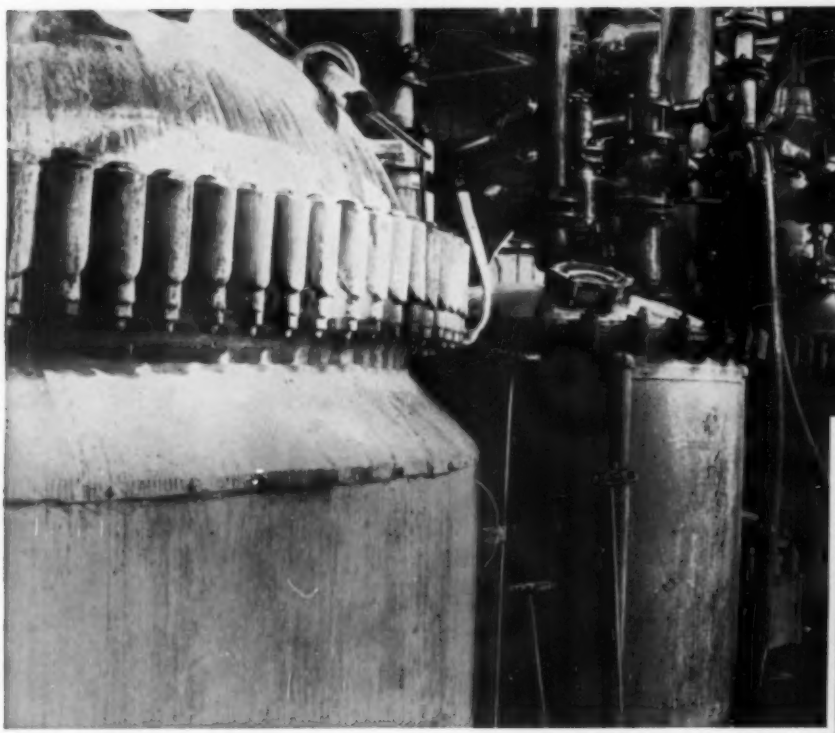
# RESINS FOR URETHANE FOAMS



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DOW Plastiatrics

DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

# STUDY EMPHASIZES ENVIRONMENT AS IMPORTANT FACTOR IN LIMITING DESIGN STRENGTH (PART 2)

(This is the concluding half of a two-part article detailing the importance, and some of the effects, of environment on the performance of plastics materials. Part 1, which appeared in a recent issue of this magazine, was concerned primarily with the roles of design and environment as important, but often neglected, elements of engineering data.)

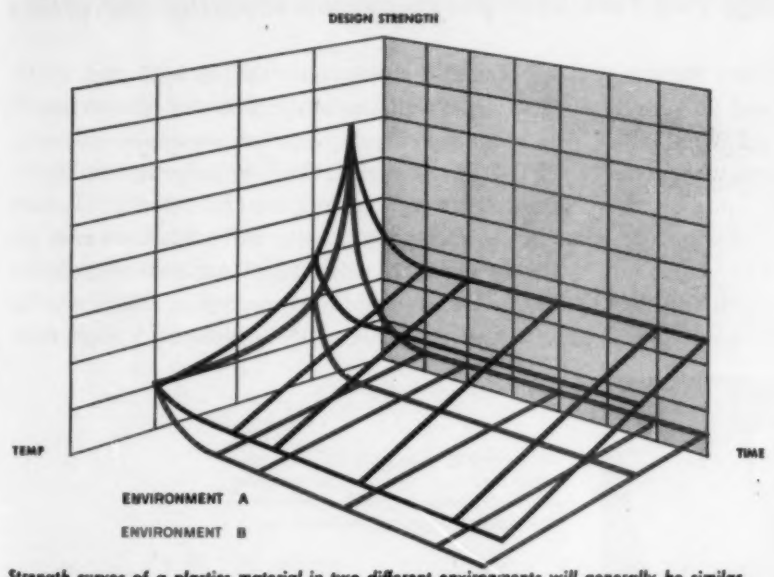
It's well known that environmental effects are commonly found in dealing with such engineering materials as metals, ceramics, and even glass. In these materials, environment sensitivity is often called "stress corrosion" or "stress corrosion cracking", and is frequently characterized by chemical reactions. Comparable failure in plastics is termed "stress cracking", though it is seldom accompanied by failure-induced chemical reactions.

In conducting this series of Plastiatrics studies, Dow Plastics Technical Service Engineers have developed evaluation methods which allow determination of environmental effects on design strength. The methods take into account time, temperature, environment and stress level; and permit the development of design data of importance to designers and plastics engineers.

It has been pointed out that environmental changes can easily reduce the design strength of plastics—that is, the stress level above which stress cracking occurs—to a point where relatively low stresses will produce failure. When a plastics material retains relatively high strength in a given environment "A", and a second environment "B" is known to reduce that plastic's strength by many times, it is seldom possible to determine the actual degree of weakening except by physical testing. However, both strength-time curves will be similar in shape. And because environmental effects are physico-chemical in nature, both curves will generally follow the rule of chemical activity increasing with temperature.

The relationship of environment to time, temperature and strength is shown by the accompanying graph, data for which was based on a completed Plastiatrics study of a Dow plastics material.

Plastiatrics studies to develop engineering data, and to investigate many phases of plastics formulation, design, molding and finishing are continually in process by Dow Plastics Technical Service Engineers. For further information on these plastiatrics studies, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Department 2105EX9.




*Strength curves of a plastics material in two different environments will generally be similar in shape, but the relative degree of strength at any specific time-temperature point can, and usually does, vary considerably.*

AMERICA'S FIRST FAMILY OF THERMOPLASTICS

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Zerlon*
Ethocel*
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Polyethylene
PVC Resins
Pelaspan*
Saran

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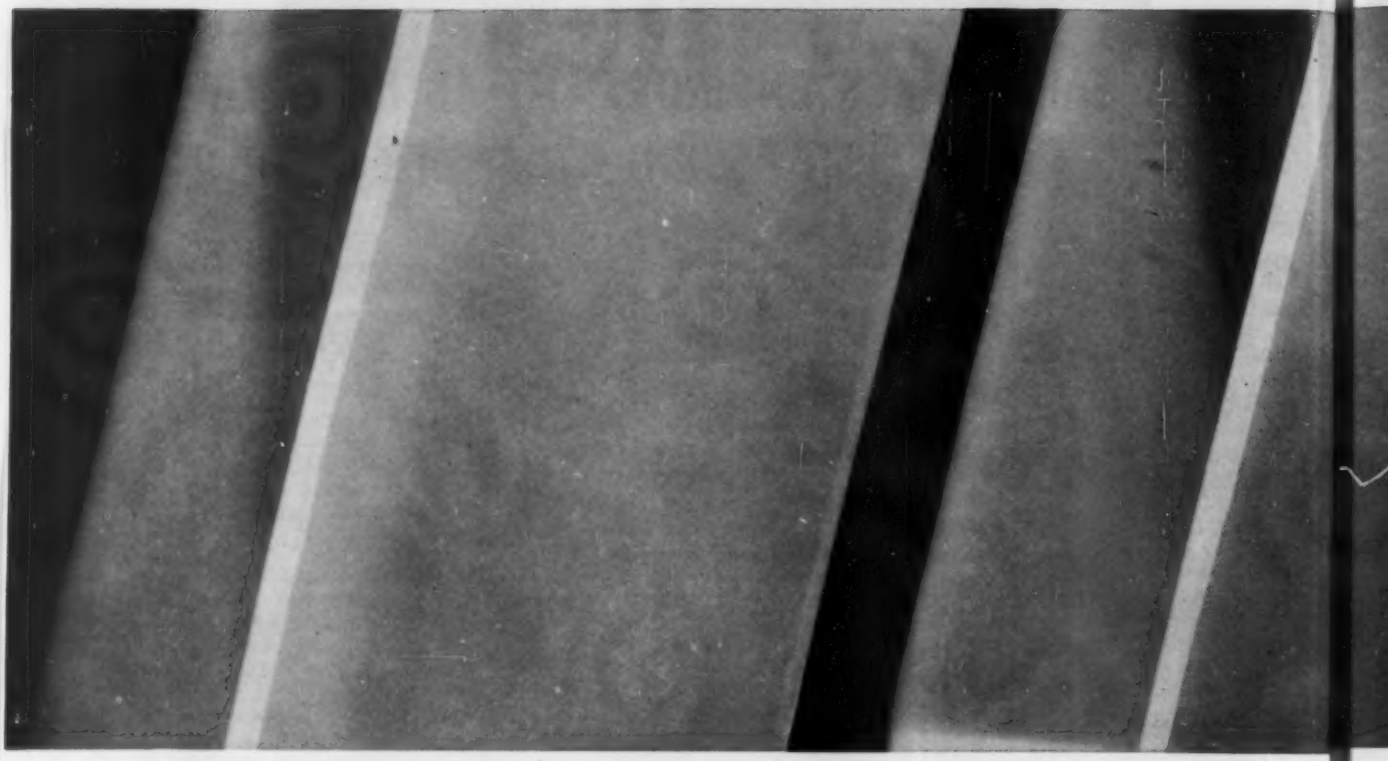
THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN

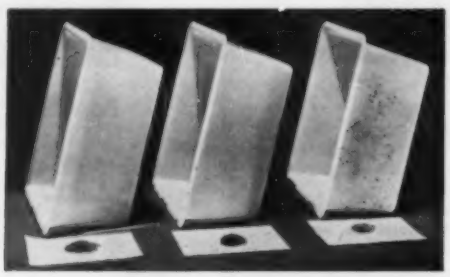
# Which polyethylene



## *UNION CARBIDE brings you two new polyethylene molding materials*

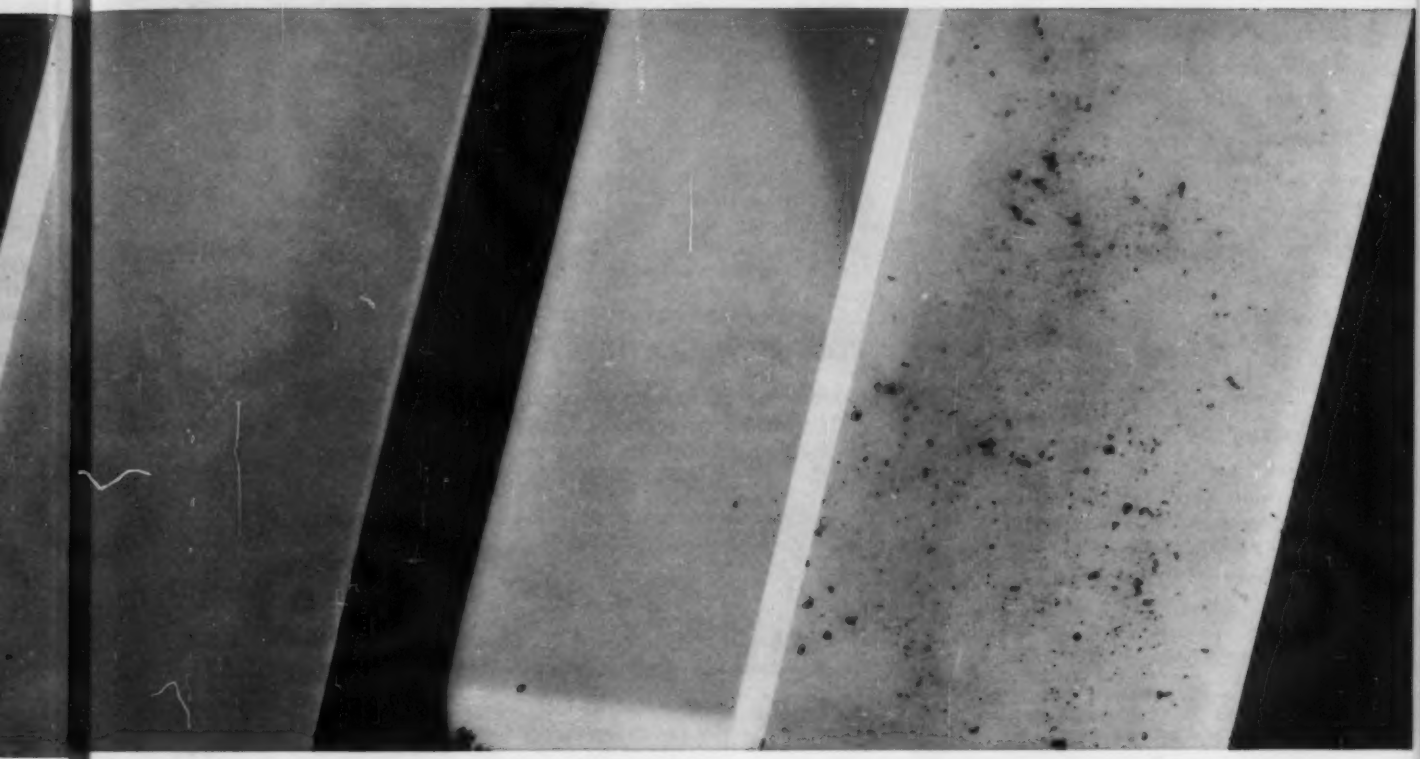
This new benefit is engineered into two BAKELITE Brand Polyethylenes—DNDA-0401 and Polyethylene Copolymer DPD-7366 Think of what this means in saving of time for retail stores, where conventional polyethylene articles take hours of constant dusting . . . and the more they're wiped, the more dust they attract! Now, colors stay bright and surfaces sparkle. Housewares made with anti-dust polyethylene are *always* ready with sales appeal.

BAKALITE polyethylene DNDA-0401 and DPD-7366 possess all the other desirable properties of high-quality polyethylene housewares compounds. DPD-7366 is based on the new polyethylene copolymer recently introduced by Union Carbide Plastics Company to the molded-housewares industry. As such, it has excellent low-temperature toughness and improved rigidity in addition to its anti-dust properties. DNDA-0401 is a high flow,



After being wiped clean, dishpans made from new anti-dust polyethylene stay dust-free (left), while conventional one picks up cigarette ash immediately.

# doesn't attract dust?



## *that do not attract dust . . . and help keep housewares clean.*

general purpose, anti-dust, housewares material with more flexibility than DPD-7366, in molded housewares items.

Find out which is best for you—and for your sales. Write for information to Dept. IS-52G, Union Carbide Plastics Company, Division of Union Carbide Corporation, 30 East 42nd Street, New York 17, N. Y. *In Canada*: Union Carbide Canada Limited, Toronto 7.

**TYPICAL PROPERTIES**

| | DPD-7366 | DNDA-0401 |
|---|---|---|
| Melt index g/10 min. | 8 | 25 |
| Secant modulus, psi at 23°C | 40,000 | 29,000 |
| Tensile strength, psi | 1600 | 1420 |
| Elongation, % | 210 | 134 |
| Yield strength, psi | 1500 | 1320 |

UNION CARBIDE

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# The Society of Plastics

## COVER

**Cover** this month is symbolic of The First National Technical Conference (NATEC) to be held at The Ambassador Hotel in Los Angeles, Calif., October 13 and 14, 1959. Complete program on page 815—Abstracts on page 816-817—What is NATEC and why—page 788.

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● The SPE Journal is Published at 215 Canal St., Manchester, N.H. Address changes, undeliverable copies and orders for subscriptions should be sent to 65 Prospect St., Stamford, Conn.

● Entered as second-class matter at the Post Office at Manchester, New Hampshire. Accepted at special postal rate provided in paragraph (d-2), Sec. 34.40, P.L. and R., of 1918.



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# THEY LOOK ALIKE, BUT ARE THEY?

## Economical Plaskon Wood-Flour Filled Urea offers greater dielectric qualities

In any electrical socket or closure, high dielectric qualities are an absolute necessity. And PLASKON Wood-Flour Filled Urea features 80-100 second arc resistance protection (A.S.T.M.). This extra insulating factor—at no extra cost—represents a sizable safety cushion for any possible emergency situation.

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In addition to dielectric qualities, PLASKON Wood-Flour Filled Urea offers: *Superior color-fastness, scratch resistance, hard non-electrostatic surfaces and remains unaffected by household solvents.*

Today—take a long step toward a switch to Wood-Flour Filled Urea. Write or phone for technical data and molded or material samples.

**PLASTICS AND COAL CHEMICALS DIVISION**
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Allied Chemical

# for a tough sign plastic...**BUTYRATE**

Durable signs, with letter faces vacuum-formed from sheets of Tenite Butyrate plastic, now identify J. I. Case Co. dealers to tractor, farm implement and industrial equipment buyers throughout the world.

Butyrate sheet's brilliant luster gives these letters an eye-catching, eye-pleasing appearance in daytime; and its excellent light transmission and diffusion properties provide long-distance legibility when backlighted at night.

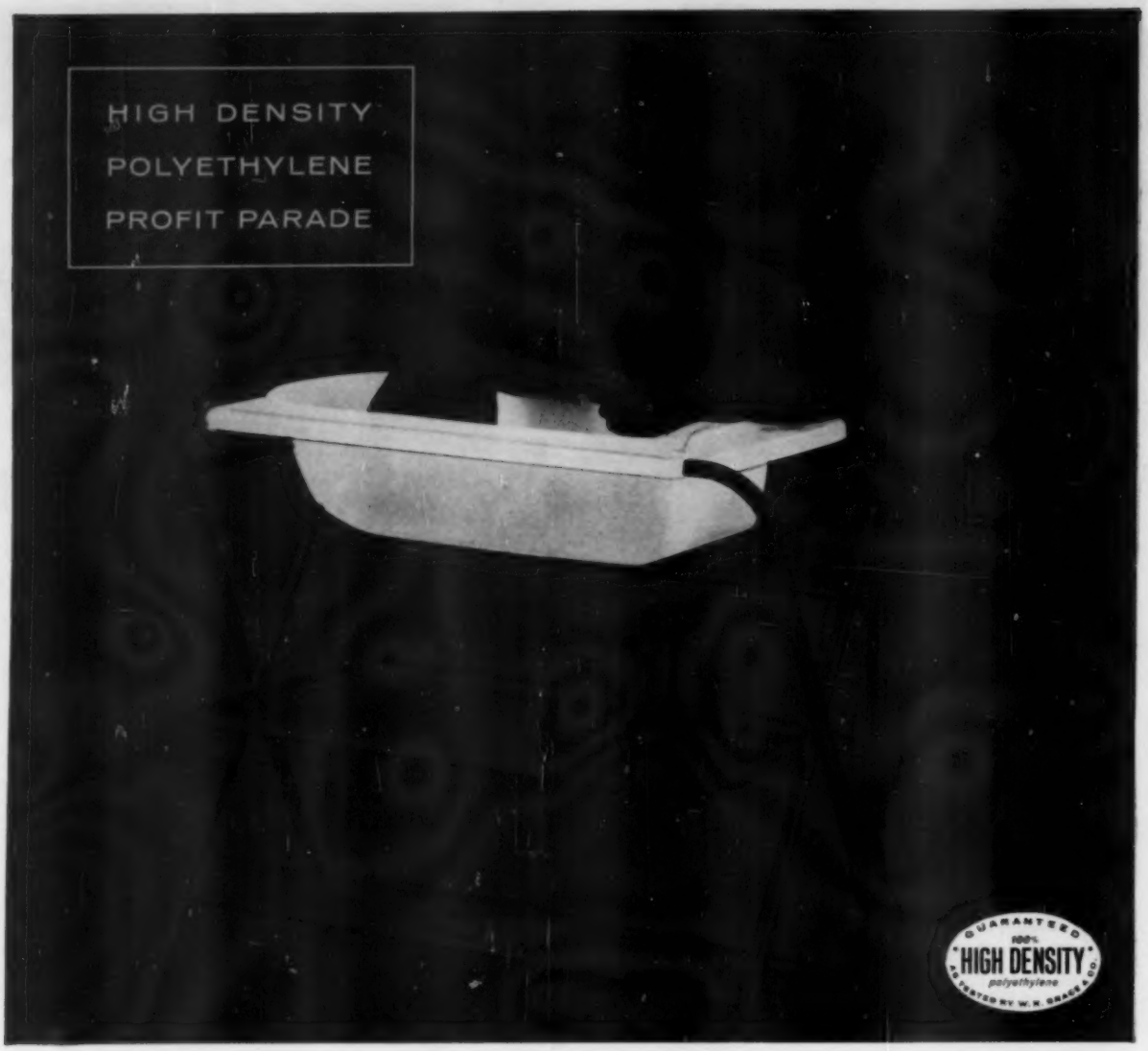
These properties, while important, were not the main reason for choosing Butyrate. Superior toughness was the big advantage Butyrate sheet offered over other plastic sign materials. Toughness was a "must" with Case, because the signs would have to endure considerable rough handling and abuse enroute to dealers, particularly those located in foreign countries. And even after reaching an overseas destination safely, there was still the possibility that inept handling by unskilled labor could result in breakage during installation. By specifying Butyrate, Case obtained maximum protection against breakage and costly, time-consuming replacements.

Another point in favor of Butyrate was its proved outdoor durability. Despite severe climates, hot or cold, the special weather-resistant formulation of Tenite Butyrate plastic used in these signs will keep them attractively bright for years.

Outdoor signs are a logical use for Tenite Butyrate, and sign men turn to this plastic when they need a tough, durable material. However, the applications for Tenite Butyrate cover a wide range of consumer and industrial uses. For more information on the performance advantages and easy-forming properties of Tenite Butyrate, write EASTMAN CHEMICAL PRODUCTS, INC., subsidiary of Eastman Kodak Company, KINGSPORT, TENNESSEE.

**TENITE**
**BUTYRATE**
*an Eastman plastic*

J. I. Case Co. signs are manufactured by Everbrite Electric Signs, Inc., 1440 N. Fourth St., Milwaukee 12, Wisc. Letter faces are vacuum-formed from extruded sheet of Tenite Butyrate plastic. Sheet is extruded by Southern Plastics Company, 408 Pendleton St., Columbia, South Carolina.




# Exclusive Selling Advantages Offered in Lifetime Tub

Products in many different fields are gaining an edge over competition by utilizing the benefits of Grex high density polyethylene. The "Lifetime Tub" by Baby Bathinette Corporation is an example that really holds water.

This well-known manufacturer chose Grex to make a tub that would outlast competitive models since this is a tough plastic that is virtually indestructible. They used its molding characteristics to obtain a soft, pleasant, easy-to-clean texture. They took advantage of its strength and rigidity to make the tub light in weight for greater ease of carrying.

This new Grace plastic offers a unique combination of properties to help you create unique selling advantages. It takes a beating without chipping, cracking or breaking. It can be molded in any color and decorated. It resists the elements and most corrosive chemicals. And it is the only thermoplastic that takes boiling or freezing without losing its shape or strength.

If you need an idea of how to gain an edge over competition by using high density polyethylene be sure to call in the experts. Grace has the production facilities, technical service and experience to help put your product in the Grex profit parade. We're easy to do business with.

*Grex is the trademark for W. R. Grace & Co.'s Polyolefins.*

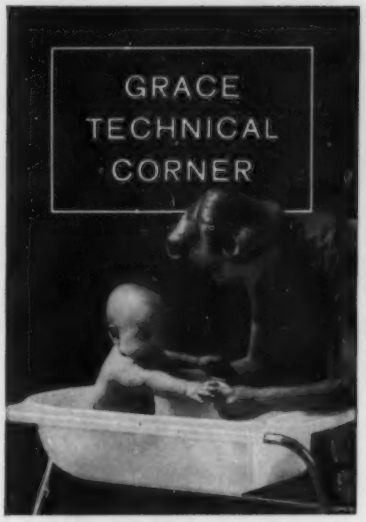
**W.R. GRACE & CO.**
**POLYMER CHEMICALS DIVISION** CLIFTON, NEW JERSEY

# THE EDITOR'S *Notebook*

## *The Quiet Revolution*

**M**ention the word revolution, and most of us immediately form a mental picture of something of great import happening overnight, possibly accompanied by force. Truth of the matter is, we are living in an age of revolution. Great changes are taking place silently all around us. What specific event or accomplishment signals its start or will mark its end is a question which can only be answered in hindsight. This we can point to, though: The plastics industry is one of the most important single factors in the new "industrial" revolution. The impact of its technical developments on our daily lives, our jobs, our buildings, our cars, is and will continue to be terrific. Look at some of the examples: We have all-plastic shoes (the subject, incidentally, of the Nov. 4, 1959 St. Louis Section RETEC); research is being conducted on the use of transparent plastics for use in electroluminescent panels—the lighting of the future; we have plastic bathtubs and yes, swimming pools; reflectorized vinyl material is being used for traffic marking, instead of paint. The list is endless; the quiet revolution never over.

As we start with this, our first issue of the SPE Journal, these thoughts of accomplishment go through our mind. The pattern set by the architects of the quiet revolution make it a privilege to become a part of this growing industry, and the professional Society which is contributing so much to this growth.


Grex answers design and molding problems on extra-large piece.

Don't let size limit your thinking when designing or molding with Grex high density polyethylene. The "Lifetime Tub" shown here is 30½" x 6½" x 19"—one of the largest pieces so far injection molded with this Grace plastic. Some of the technical thinking that went into this job may give you an idea of how to get the most from Grex.

*Cost a design factor.* Production of a piece as large as this tub invariably presents a cost problem. Taking advantage of the way Grex performs in thin wall sections, the designers were able to keep the amount of resin per tub to a minimum and permit economical cycle times. Use of thin walls, however, called for a design that would not only take care of the weight of baby and water but also provide for satisfactory suspension of the tub in its metal frame. Reverse curves solved both problems and minimized use of ribs and fillets to avoid heavy sections, sinks and depressions.

*Mold surface.* Depending on mold surface, Grex takes any finish ranging from high gloss to matte. In this case, it provided a smooth, pleasant texture—essential to protect baby and make cleaning easy—through the use of a highly polished chrome-plated mold.

*Molding technique.* Production of the tub involved a 3-pound shot of Grex, a large mold cavity and thin wall sections. Under these conditions, multigating was chosen over normal gating. With four gates the cavity was filled faster and strain reduced.

*What are your problems?* If you have a job in mind for high density polyethylene count on Grace for help. Now's the time to call, wire or write:

Technical Service Department,
Polymer Chemicals Division,
W. R. Grace & Co., Clifton, N. J.

# You'll find these stimulating articles in September's MODERN PLASTICS

**What About Flame Resistant Plastics?** Lead story reviews the multitude of codes, tests and standards which have been established relative to flame resistant plastics. Outlines the vexing problems the plastics industry faces in making self-extinguishing resins, and details what has been accomplished to date.

**These Fabulous Panels.** Exciting new plastics sandwiches are adding new dimensions to architecture and decor. The sandwiches consist of translucent reinforced plastics skins with their variety of decorative cores (wood curls, honeycombs, sliced tubing, etc.) This article gives construction details, points out areas of application.

**Injection Molding — Rheological Interpretation.** (Engineering Section). Now—the first comprehensive, basic quantitative study of the flow of polymer in the injection process and its effect on the various molding conditions.

**Premix Problems — Part 4.** (Engineering Section). Final article of four-part series tells what to do about poor fill, deflashing small parts, mold maintenance.

**Effectiveness of Coupling Agents in Glass Reinforced Plastics.** (Technical Section). What happens when vinyl silane coupling agent is 1) omitted; 2) added in resin solutions; 3) applied to the glass surface in glass reinforced plastics? Article relates surprising conclusion that under certain conditions better copolymerization can be obtained with vinyl silane; also that the adhesion of the coupling agent and the glass is a more significant factor in terms of strength than coupling with a resin.

**Polystyrene for Lighting Fixture Use.** (Technical Section.) An important consideration in establishing suitability of a material for lighting fixture use is the effectiveness of UV stabilizers and antioxidants incorporated in formulation. This article outlines accelerated test procedures which will predict with reasonable accuracy the expected useful life of a light-stabilized polystyrene.

**Plus many interesting "applications" stories not listed here.**

## Coming in October:

**Extruder Without a Screw.** An unusually significant MODERN PLASTICS "first", this article describes a screwless extruder prototype that is expected to vastly reduce machine size, and reduce to seconds the time the material stays in the machine. The transportation of material is based on a new design using the centripetal pumping action resulting from the rotary shearing of viscoelastic melts.

**Plastic Glazing for High-Speed Aircraft.** Aircraft and spacecraft design feasibility has progressed sufficiently to require glazing for steady state temperatures of 350°F and transient temperatures up to 1000°F. This article presents a solution to glazing problems of current and future designs through the use of a composite transparency structure involving stretched acrylic.

## New Encyclopedia Issue

Mailing of the new MODERN PLASTICS ENCYCLOPEDIA ISSUE for 1960 to regular subscribers will begin shortly. The only publication of its kind in the world, it numbers 1,242 pages and covers every phase of plastics engineering, design, production, technology and materials selection.

A BRESKIN PUBLICATION

**MODERN PLASTICS**

*AUTHORITY OF THE FIELD FOR 36 YEARS*

U.S.I. POLYETHYLENE NEWS

A series for plastics and packaging executives by the makers of PETROTHENE polyethylene resins

## Packaging Notes

**New polyethylene bag-making machine** is capable of sealing polyethylene film up to 10 mil thick. The machine reportedly has better temperature control instrumentation than conventional machines. Sealing bar pressure is controlled pneumatically. Control of pre-dwell, dwell, and post-dwell times is by separate timers and the film is sealed in a completely relaxed state.

The machine can convert both blown tubing and flat film into bags. Its production rates are said to be comparable to other bag making machines.

---

**Wafer-thin snap fasteners for polyethylene envelopes** are now finding use in packaging retail soft goods. The fastener keeps the package closed, protecting the product, yet allows the customer to inspect the packaged product.

---

**Freeze-it-yourself popsicles** packaged in polyethylene-coated cellophane are now on the market in some parts of the country. The popsicles are sealed in pouches in liquid form for freezing at home. After freezing, the popsicles may be separated from each other and eaten by squeezing them out of the pouch. No sticks are needed. The film, cellophane with a 2-mil coating of polyethylene, is supplied in both printed and unprinted webs, generally four across for twin popsicles. The cellophane is printed before coating with polyethylene, locking in the printing.

---

**Label adhesive** for plastic surfaces is said to stick where average adhesives will not hold. It reportedly replaces pressure sensitive adhesives, which are slower and more costly to apply.

The adhesive is waterproof and permanently flexible. It will adhere to polyethylene, yet can easily be removed. The adhesive is applied by brush or automatic machine.

---

**Polyethylene toothpaste tube** has been developed. It is produced by an extrusion-injection molding method. A special coating is said to guard against loss of flavor and essential oils by permeation.

---

**New flexible polyethylene bag** with a sealed-in plastic tube serves as a "drink-from-the-package" container for fruit and vegetable juices, milk, soup, and soft drinks. The ready-to-use container simplifies disposal problems, speeds cooling, and is suitable for use in vending machines.

# U.S.I. Develops Three New Resins With Improved Coating Properties

### New PETROTHENE Resins Have Better Adhesion, Reduced Neck-in

U.S.I. has announced the availability of three new PETROTHENE polyethylene resins especially suited to paper coating. These new resins were developed in U.S.I.'s Polymer Service Laboratories and have successfully undergone extensive field testing.

The new resins show a marked improvement in adhesion to paper and other substrates. They also have shown reduced neck-in, smoking and polymer build-up at the die.

Neck-in, in particular, has been a troublesome problem in paper coating. It occurs when edges of the hot polymer web "neck" inward, carrying a thickened bead onto the paper. Neck-in results from a combination of resin properties and extrusion conditions. The new resins minimize the polymer's role in causing neck-in.

The resins are recommended for extrusion in the 575°-600°F. range, and cover a wide range of coating weights as shown in the chart at left.

U.S.I. COATING RESINS

| PETROTHENE Resin | 203-2 | 201-2 | 200-2 |
|---|---|---|---|
| Melt Index | 8.0 | 5.0 | 3.0 |
| Density | 0.915 | 0.915 | 0.915 |
| Coating Weight | 3-15 lb. per 3,000 sq. ft. | 10-25 lb. per 3,000 sq. ft. | 20 lb. or greater per 3,000 sq. ft. |

## Polyethylene-Coated Cup Is Tasteless, Odorless

A polyethylene-lined paper cup for hot drinks is reported to be completely tasteless and odorless. The coating eliminates sidewall staining and penetration.

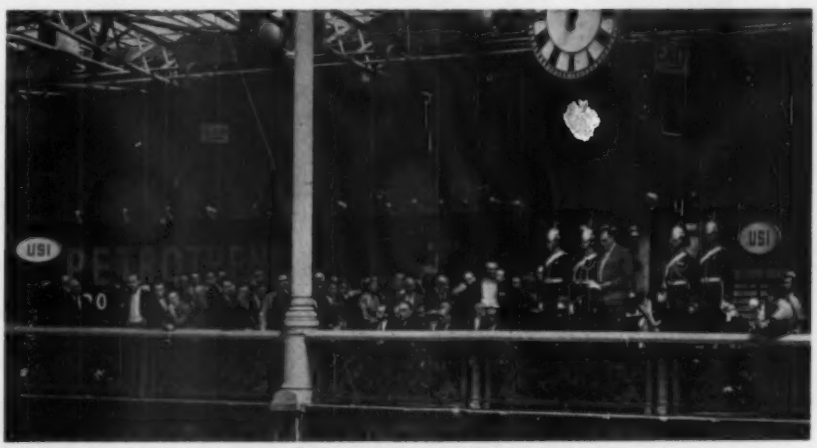
While ordinary plastic-coated paper cups are sprayed with material after they have been formed, the new cup is constructed from paper pre-coated with polyethylene. No glue is used in construction. The polyethylene itself serves as a seal for the seam and bottom, creating a bond that cannot be separated without tearing the fibers of the paper. The coating is said to be bonded firmly enough to the substrate to permit water to be boiled in the cup without damage to the cup lining.

The single wrapped cup nests closer — saving about one-third of the storage space normally required. The cup is available in six and eight ounce sizes, with or without handles.

## New Package For U.S.I. Electrical Grade Resins

U.S.I. electrical grade PETROTHENE polyethylene resins are now being packaged in fifty-pound bags made of 10-mil polyethylene upon request. The bags provide added protection from moisture for the carbon-black compounded electrical resins which tend to pick up water vapor from the air.

## U.S.I. at the International Plastics Exhibition




U.S.I.'s booth at the International Plastics Exhibition was the background for the opening ceremony, June 17th in Grand Hall, Olympia, London. Above, the Exhibition is being addressed by The Right Honourable Reginald Maudling, Paymaster-General, who stands between trumpeters of the Royal Horse Guards.

exceptional moisture and grease resistance

# POLYETHYLENE-COATED KRAFT OPENS UP NEW OPPORTUNITIES FOR CORRUGATED BOARD

Polyethylene-coated corrugated board — produced on conventional corrugating equipment — is extending the usefulness of corrugated into many new packaging applications.

This unique container board has exceptional moisture and grease resistance and a glossy, non-abrasive liner surface that will not scratch or mar package contents.

Extruders who produce polyethylene-coated kraft liner board can get these extra advantages by using U.S.I. PETROTHENE® polyethylene resins:

**HIGH PRODUCTION RATES**—PETROTHENE resins have good drawdown properties, permit extrusion at high speeds.

**EXCELLENT ADHESION** — with minimum hot melt oxidation.

**NO ODOR** — an important consideration in many packaging applications.

Contact U.S.I. for information on PETROTHENE resins especially suited for coating kraft liner board.

**Packagers are investigating polyethylene-coated corrugated board for applications like these:**

Bulk shipment of meat, where moisture and grease-proof interiors reduce weight loss of the meat and keep moisture from weakening the carton.

Shipment of furniture and other hard goods, where abrasion damage from the container has been a problem.

Bulk bakery and confectionery shipments, where absence of grease-wickage makes containers suitable for reuse as point-of-sale displays.

In concrete construction forms, where the polyethylene coating acts as a release agent.

U.S.I. INDUSTRIAL CHEMICALS CO.
Division of National Distillers and Chemical Corp.
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*Branches in principal cities*

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POLYETHYLENE RESINS

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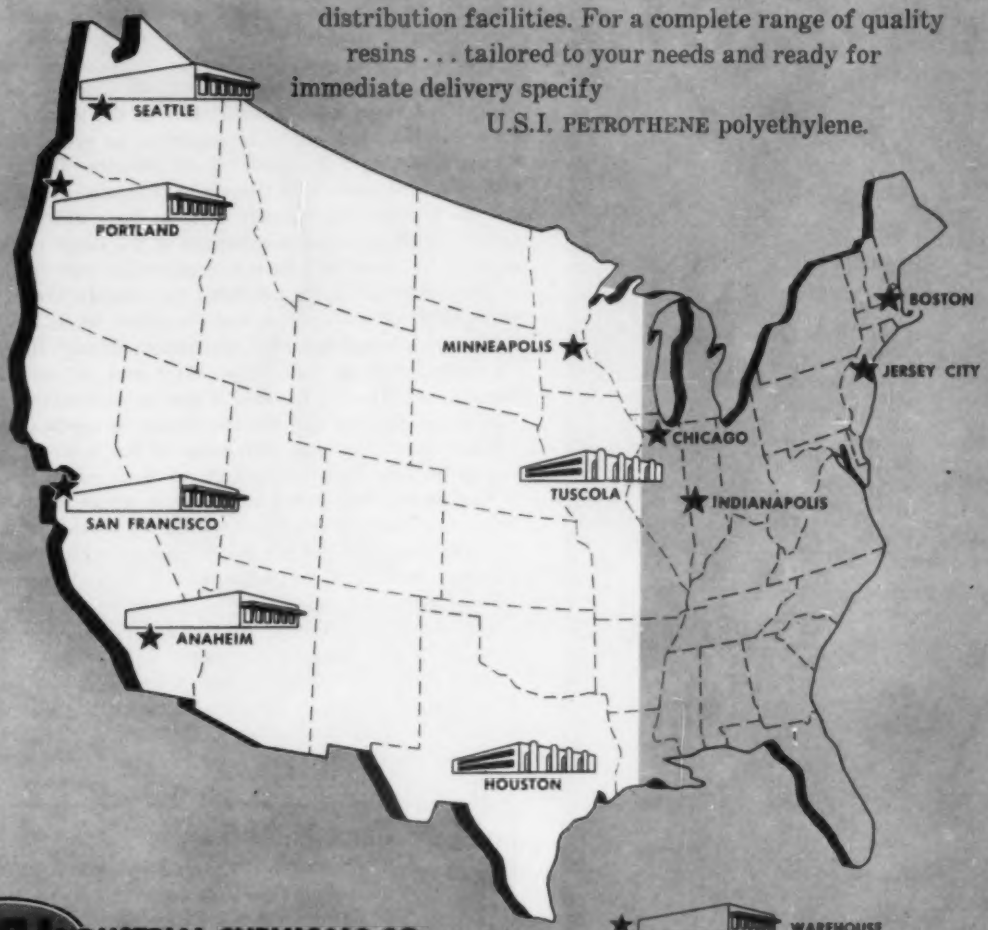
U.S.I. serves the West with quality PETROTHENE® polyethylene resins from four convenient supply points. These are backed up by nationwide production and distribution facilities. For a complete range of quality resins . . . tailored to your needs and ready for immediate delivery specify U.S.I. PETROTHENE polyethylene.

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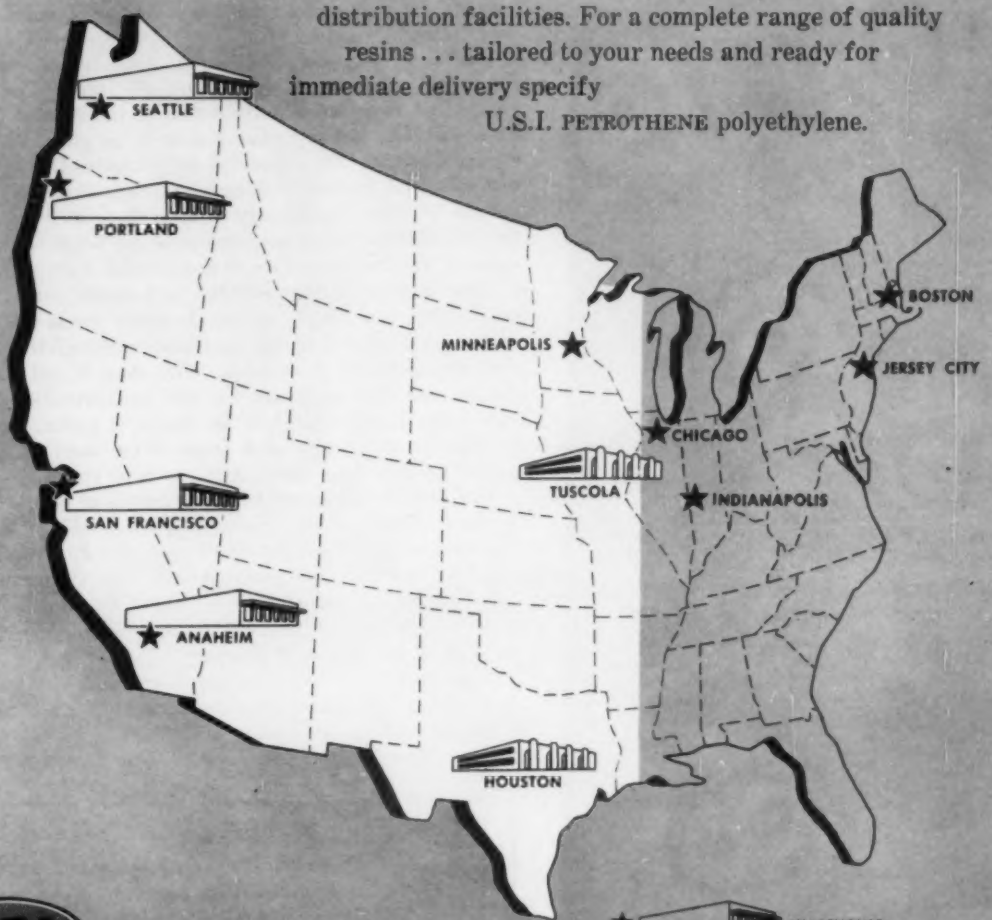


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**1st NATEC—October 13-14, 1959,**
**The Ambassador Hotel, Los Angeles, California**

# Plastic Engineering—The State of the Art Today

## What is NATEC and Why?

**Jack A. Fuller, General Chairman, 1st NATEC**

A NATEC is a National Technical Conference differing from the ANTEC (Annual Technical Conference) only in not having the Annual Business Meeting and election of officers which traditionally take place at ANTEC. A NATEC is a full-blown technical conference of national scope and appeal.

NATEC has come into existence because of the very obvious need for another vehicle to encourage the preparation and publication of technical papers on the many facets of plastics engineering. And this, after all, is the very purpose of the Society of Plastics Engineers—to promote the preparation and dissemination of engineering information relating to plastics.

There has been considerable talk and editorial comment recently about the frequency of conventions and conferences of our plastics groups and some have believed that in the interest of filling a program, we have allowed some papers to be given which were below standard or simply a rehash of old subjects. This could be entirely true and thank heaven for those who recognize it and speak out loudly enough to warn the industry to keep their standards up! There are enough intelligent data pouring out of the heads of our leading engineers so we should not have to compromise with quality.

These data are being produced in a steady stream and should be so reported in a steady stream. It seems much more reasonable to space two national technical conferences through the year and handle the information as it develops. Why store it and stifle it for many months and then try to cram it into an overstuffed engineer in four days every January and run the chance of spoiling some of the food because it sat too long with some of the daintiest of morsels overlooked because there just wasn't any more room?

Our Society has grown to the point where our ANTECS are very large. It is the opinion of most that we would get more from these Conferences if we did not try to give an entire year's papers in one four-day meeting. Two geographically separate meetings would give more people an opportunity to attend the National sessions more economically. All of this will be accomplished by the addition of NATEC to our technical activities.

Attend the 1st NATEC in Los Angeles! We have selected twenty-five topnotch papers to bring you up to date on "Plastics Engineering —The State of the Art Today," and besides all this, we have a beautiful and vigorous city to show you. The picture at left is proof.

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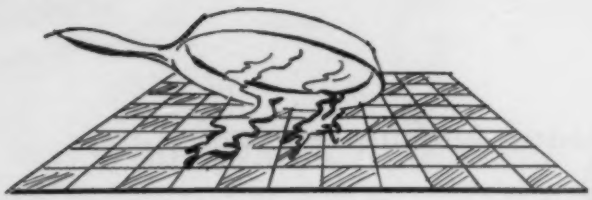

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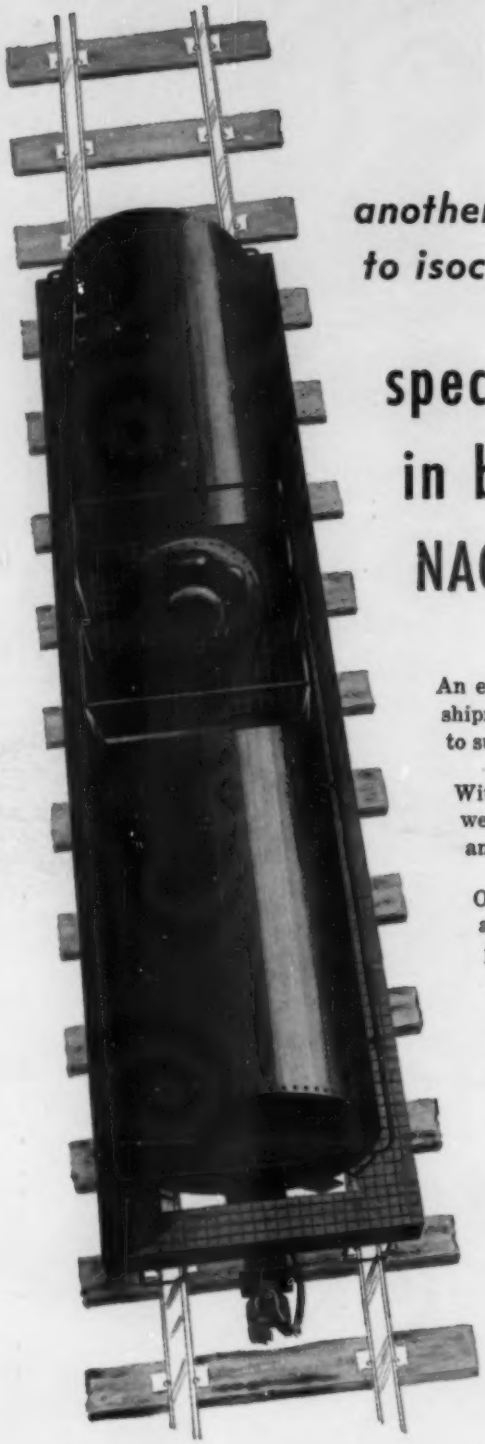

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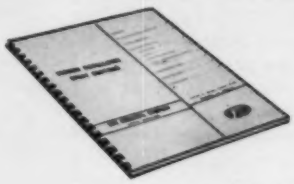

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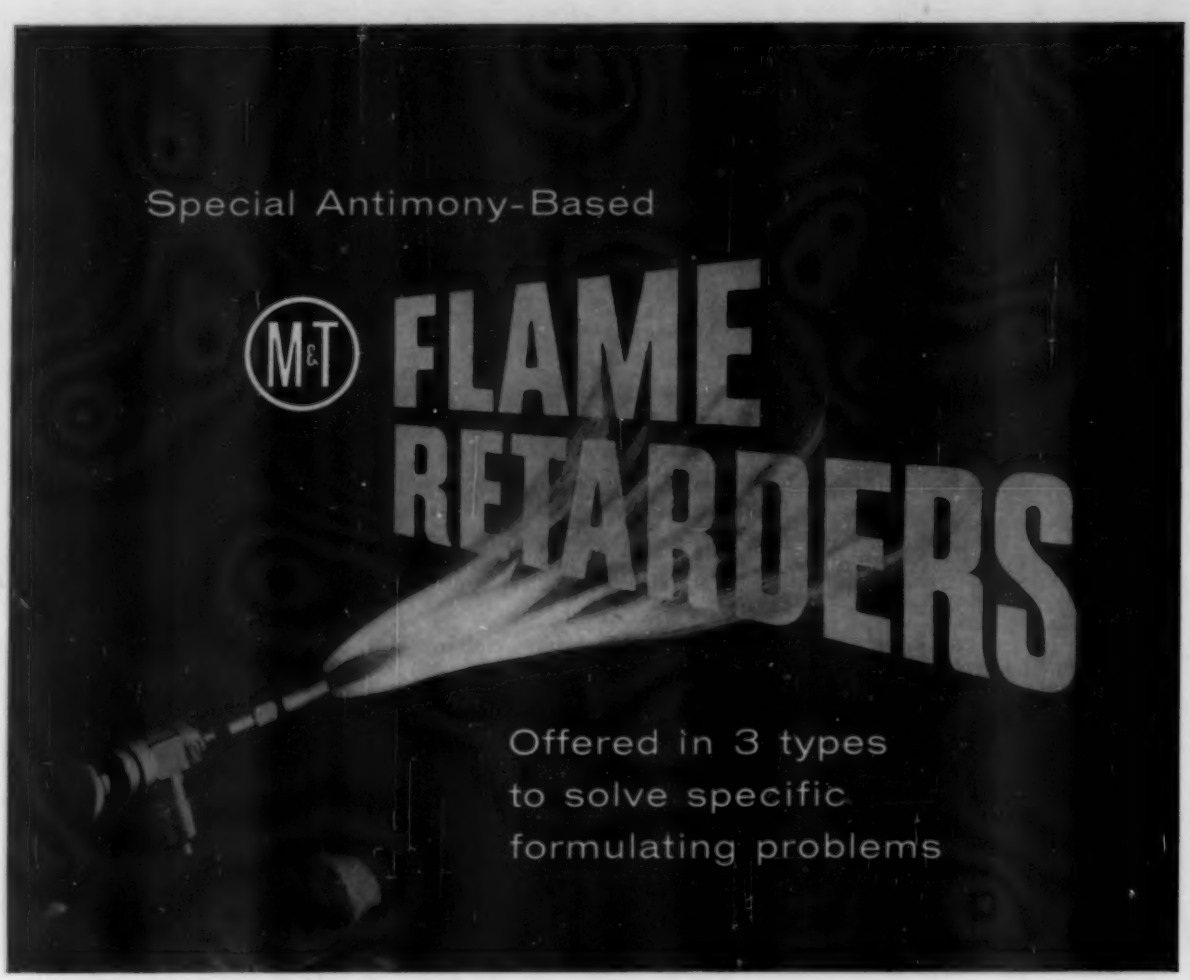


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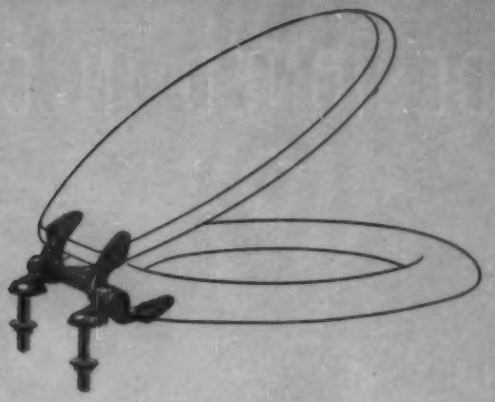

# C. F. Church selects MARLEX* for revolutionary new toilet seat hinge

**"We picked MARLEX rigid polyethylene for this component because it combines economy with all of the qualities needed in a hinge of this type . . . toughness, unbreakability, resistance to corrosion and bacteria . . . self-lubrication, rigidity, hard glossy surface and colorability."**

This new MARLEX hinge represents the first major improvement on the conventional brass bar hinge, which has been used by the plumbing industry for almost one hundred years. Like so many manufacturers, the C. F. Church Division of American Standard recognizes that in MARLEX they have a material that can successfully replace metals, glass and wood, as well as more expensive plastics such as nylon, in thousands of component applications.

*No other type of material serves so well and so economically in so many different applications. How can MARLEX serve you?*

*MARLEX is a Trademark for Phillips family of olefin polymers.

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MARLEX® PHILLIPS 66

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Hose manufactured for Eureka Williams Corporation, Bloomington, Ill., by Lawrence Hose Company, Trenton, N. J. Fortiflex filament, Reevon, supplied by Reeves Brothers, Inc., New York 18, N. Y.

## Hose armored with Fortiflex filament helps Eureka make tough cleaning jobs go lightly

Because the outer braid is woven of Celanese Fortiflex filament, this hose is strong and abrasion-resistant. It's easier to use—lighter, more flexible—thanks to the thin wall section made possible by the high strength of Fortiflex. Smooth, colorful, with a handsome pattern in the weave and a surface that is easily cleaned, this hose typifies the advantages Fortiflex filament has to offer designers.

Fortiflex, a linear polyethylene, has much greater stiffness, hardness, strength and heat-resistance than the chemically-similar soft polyethylenes. For example, it can be sterilized in boiling water. Filaments drawn from this material have high tensile strength, toughness and durability. The high tenacity of the filament is partly due to a multiple stretching process. This orients the molecules, aligning them in the direction of stress. The high strength of the filament is accompanied by low elongation and excellent low-temperature resistance. Here is a design material which is ideal for making hoses, automotive seat covers, outdoor furniture webbing,* industrial filter cloths, fishing nets* and many other products.

Celanese supplies Fortiflex plastic for further processing into fibers. We'll be glad to put you in touch with manufacturers who produce and sell the filament, and we welcome inquiries as to properties and applications of Fortiflex filament. Simply clip and send us the coupon at right.

Celanese® Fortiflex®

**TYPICAL PROPERTIES OF FORTIFLEX FILAMENT**
(12-mil gauge)

| | |
|---|---|
| Specific Gravity | 0.950 to 0.960 |
| Tenacity (grams/denier) | 4.5 to 8.0 |
| Tensile Strength, psi | 55,000 to 100,000 |
| Elongation, per cent | 14 to 30 |
| Knot Strength, psi | 40,000 |
| Loop Strength, psi | 60,000 |
| Water Resistance | Excellent |
| Ultraviolet Stability | Good* |

*When properly pigmented and stabilized

**Fortiflex...a Celanese plastic**

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SPE Journal

VOLUME 15, NUMBER 9, SEPTEMBER 1959

J. N. Scott, D. L. Peters, P. J. Boeke

*Phillips Chemical Company, Bartlesville, Oklahoma, Plastics Sales Division*

# Insulated Runner Systems for Injection Molding

*A recent development in mold design principals and molding technique described as "Insulated Runner Molding" combines the desirable features of three-plate and hot runner systems. This new technique greatly facilitates injection molding operations and results in savings in initial mold costs and increased production rates.*

Recent experimental work with linear polyethylenes has resulted in a new development that permits appreciable economy in both mold construction and operation. This technique, called "Insulated Runner Molding", is ideal for multicavity, center gated items or for the multigating that is sometimes necessary with polyethylenes.

## A New Molding Technique

Standard three-plate mold and several designs of hot runner molds are widely used for linear polyethylene with both systems offering certain advantages and disadvantages. Design and construction costs are usually considerably lower for the three-plate molds and temperature control and "line-out" are comparatively easy. On the other hand, they are usually somewhat cumbersome to operate and automation is difficult.

Where production quantities justify additional cost, hot runner systems are often preferred. Automation is usually easy since no runner system is ejected and trimming is eliminated. This speeds up production and saves the cost of reprocessing material. Distinct disadvantages are the higher cost and frequent difficulty in "lining-out". Major difficulties with hot runner molds are related to the fundamental problem of keeping the runner system near cylinder temperatures and the gate area cool to permit short cycles and to prevent warpage and gate brittleness of molded parts. On the other hand, adequate cooling of the mold in the gate area will frequently freeze the resin in this section of the runner. Good insulation between the runner system and the mold cavity would eliminate many of the problems normally associated with these molds.

A new molding technique combining the desirable features of hot runner and three plate operations has recently been developed. This technique employs the excellent insulating properties of the linear polyethylenes to keep the material in the runner system of a three-plate mold molten and near operating cylinder temperature. With the low thermal conductivity and high specific heat of these resins, the center core of a large diameter runner does not change temperature significantly during production, particularly if this core is completely displaced by hot resin during each cycle.

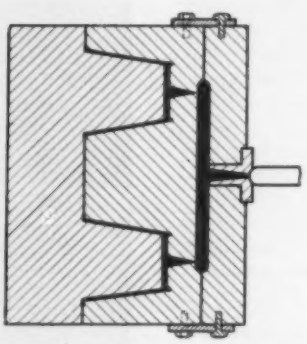

**Figure 1.** Example of 3-plate mold converted to heaterless insulated hot runner system.

Initial work was carried out on three-plate, container molds. Very minor modifications consisted of increasing the ¼-inch diameter runner to ⅜ inch full round and locking the two front plates of the molds together by simple strap latches, (Figure 1). One of the molds was constructed to leave a short sprue on the part (Figure 2A) while the other design allowed breaking of a gate at the surface of the part (Figure 2B).

During the start-up of the operation, the outer portion of the runner froze almost immediately and in a very short time the thickness of the solid "skin" reached equilibrium with the inner portion of the runner remaining molten from one cycle to the next. The center of the runner was effectively the same as a "hot runner" without the difficulty normally associated with proper balance of heat in the hot runner system and the cavity. This simple design was considerably less expensive than the construction of a heated runner system, and no difficulty was experienced in operation over a wide range of cylinder temperatures and cycle time. In order to prevent short shots on the start-up, it was necessary to meter in the extra amount of material that is required for the oversize runner prior to making the first shot. Subsequent shots could be either starved or packed depending on the requirements of the part being molded.

Of the two types of gate design shown in Figure 2, type "A" allowed better temperature control of the cavity in the gate area. The "B" design eliminated the necessity of a trimming operation. Details of gate bushings for these two are shown in Figure 3. The tapers shown were found to be minimum for satisfactory performance.

## Advantages

In order to better visualize the operation and determine the dimensions of the molten portion of the runner, changes in resin color were made after the cycle had been well established. Longitudinal

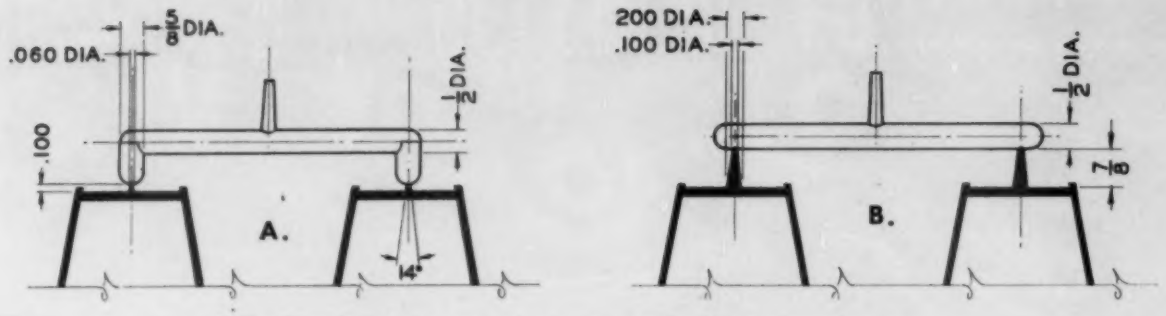


**Figure 2.** A. Insulated runner short sprues. B. Insulated runner long sprues.

cross-sections of these runners (Figure 4) clearly show the sections that were solid and molten during the operation. The insulating outer shell of the runner (white area), frozen during the first few shots, remained in place permanently while any number of shots could be made through the molten inner portion of the runner (dark area) without noticeable erosion of the solid shell.

The insulating shell thickness at three places in this typical runner system was:

| | |
|---|---|
| *Main body of the runner* | *0.100 inch* |
| *Main sprue* | *0.030 inch* |
| *Ends of the runner (dead spot)* | *0.435 inch* |

The thickness of the solid section was increased slightly by increasing the cycle time; adding ten seconds to the clamp time on the cycle added from 0.015 to 0.030 inches to the thickness of the insulating shell of this ¾ inch runner.

Further experimentation indicated that runner diameters up to one inch were sometimes desirable to increase pressure transmission to the gate and to improve resin temperature uniformity. These large runners considerably increased filling ease and speed over the relatively small diameter runners normally necessary for satisfactory three-plate mold operation. With the large runners, the cross-section of the molten core appears to be dependent to some extent on the size of the sprue and gate openings in addition to the cycle time and material temperature.

Since this initial work, several three-plate molds have been successfully converted and many new molds have been designed and built for "insulated runner" type of operation. As would be expected, conversion of three-plate molds, in addition to offering the advantages already mentioned, also reduced machine size requirements. The plasticated resin necessary for molding a given item was reduced by an amount equal to the cold runner and sprue. Frequently, this was a large percentage of the total shot. Also, mold space and stroke requirements were reduced by the distance normally needed for removal of the cold runner. This was found to be very significant in that an item with approximately two to three inches deeper draw could be molded on a given machine.

The insulated runner technique is readily adapted to most multicavity or multigated molds where the displacement of molten material through the runner is at least equal to the volume of the ¾ inch diameter center core. It can also be used to advantage on single-cavity sprue-gated items where mold space and clamp stroke are critical. Perhaps the most important area of application is for large multigated items. With linear polyethylene items that exhibit warpage tendencies or that are difficult to fill, multiple gating has frequently been a necessity. Through the use of "insulated runner" design, it is possible to multiple-gate many of these items without significant increase in costs.

Insulated runner molds offer tremendous savings in initial costs, production time, and resin reprocessing expense. These molds provide a trouble-free technique for producing superior molded items at lower cost on conventional equipment.

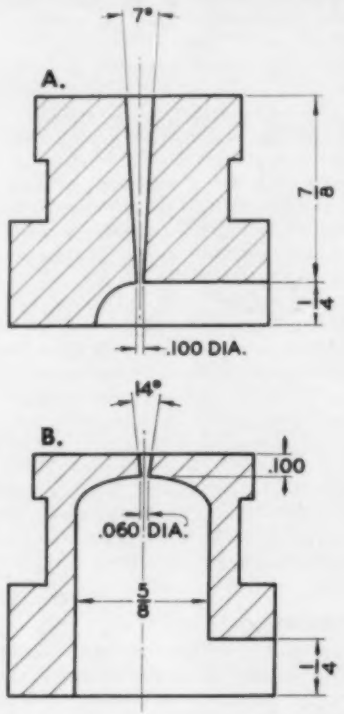


**Fig. 3.** A and B. Bushing design for insulated runner system.

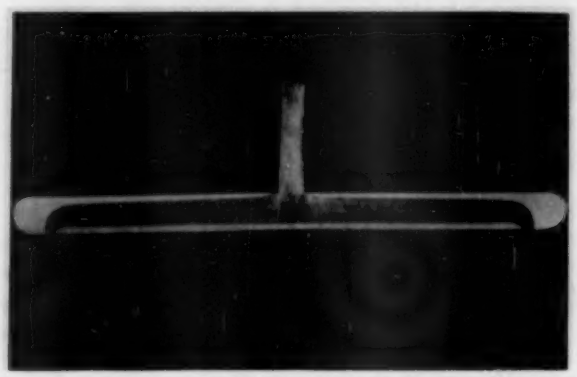

**Figure 4.** Insulated runner (longitudinal cross-section). White area: insulating shell of solidified polymer. Dark area: molten "working" polymer.

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*This article illustrates the effectiveness of oxygenation in PVC discoloration, suggests how these oxygenated groups originate, and relates the presence of these color bodies to the presence of zinc and cadmium.*

# Stabilization of Mixtures Containing Polyvinyl Chloride

The conventional theory of degradation and stabilization considers that the idealized linear PVC molecule consists in its pristine form of an alternation of $-CH_2-$ and $-CHCl-$ groups forming a long chain. On subjection to heat, H and Cl atoms attached to neighboring carbons, split off forming HCl, and leaving behind a double bond. Further heating results in further dehydrochlorination. The conventional theory holds that the effect of the double bond increases the likelihood of the loss of the so-called allylic chlorine. The dehydrochlorination thus proceeds along the chain in what has been called "the zippering effect, creating an increasingly long sequence of alternating single and double bonds.

$$\begin{array}{cccccccccccc} & & & & & & & & & & & \\ & H & & H & & H & & H & & H & & H \\ -C & = & C & - & C & = & C & - & C & - & C & - \\ & & & & & & & & & H & & Cl \end{array}$$

This conjugated system absorbs light of wavelengths which increase as the number of conjugated bonds increases. The light absorption for short sequences is detectable only in the ultra-violet portion of the spectrum, but long sequences absorb visible light, and thus account for the yellow and red colors of degraded polyvinyl chloride.

**The conventional theory holds further that the HCl, removed from the degrading molecule, acts to accelerate further degradation, and that this "autocatalytic effect" accounts for the relatively rapid intensification of discoloration after a preliminary period of very little color change.**

## Applications of the Conventional Theory to Stabilizer Practice

What were the consequences of this theory in the practical field of stabilization? In the *first* place, one could try to impede the progress of dehydrochlorination. Apart from reducing the temperature, the obvious method was the removal of HCl, since the "autocatalytic effect" was the main chemical variable affecting the rate of degradation. There was thus a class of stabilizers recognized as HCl – acceptors. These included epoxy compounds, metal oxides, basic salts, and soaps of various descriptions which vied with one another on the basis of HCl–acceptance efficiency, as well as such other properties as compatibility in the vinyl compound, toxicity, sulfur stain, etc.

The *second* assault on the discoloration of vinyls due to degradation was based on the breaking up of the conjugated polyene sequence by addition, or by scission. The organotin stabilizers are reported to have been effective in this area, since they appeared to have reduced discoloration without reducing dehydrohalogenation.

**These concepts—polyene formation by zippering, HCl acceptance, and decolorizing operations on the polyene chain are the essential features of the conventional theory.**

## The Decline of the Conventional Theory

The conventional theory was impressively successful in practice. As long as resin quality was poor by present standards, and a certain amount of discoloration in vinyls accepted as normal, all of the effective stabilizers, (with the probable exception of organo-tin compounds), competed on the basis of what can be regarded as "long-term stabilization." As both stabilizers became lighter and lighter. Faint yellowing became objectionable, and optical clears and snow white opaque stock became test formulations for new stabilizers. Cadmium and zinc compounds became quite prominent in this role. But, cadmium and zinc did not correspond to the conventional theory of stabilization.

Arlman (1954) demonstrated the need for the oxygen and a catalyst (like iron chloride) before he could obtain the rise in dehydrochlorination rate previously attributed to autocatalysis. This pointed up the importance of the observations made earlier on the presence of carbonyl groups in degraded polyvinyl chloride. These oxygenated structures are irrelevant to the conventional theory.

Achhammer's (1952) early observations on the presence of hydrogen in the gases evolved by degrading polyvinyl chloride, remained almost without comment despite their theoretical importance.

Winkler (1957) pointed out that conjugation of double bonds would tend to stabilize rather than activate the allylic carbon, thus questioning the importance of the "zippering" theory. He offered oxidation as evidence of free radicals and suggested that dehydrochlorination is a free-radical reaction.

## The Problem of Zinc and Cadmium Stabilizer Performance

An important clue to the nature of the problem is obtainable by studying the differences in performance of basically differing stabilizers.

Systems stabilized with Zn and Cd soaps undergo much less discoloration in the early stages of heating than do systems stabilized with, let us say, Ba soaps. However, the rate of deterioration, when it finally occurs, is very rapid, and an intensely black product is easily obtained. In some cases, it is so rapid, after discoloration begins, that it is impossible to find an intermediate stage between non-discoloration and black.

It follows, therefore, that color is an insufficient clue to the history or state of the vinyl compound. For an undiscolored compound in the Ba– stabilized system may turn light yellow on further heating for 30 minutes, while a similarly undiscolored compound in the Zn– stabilized system, may turn black in a few seconds.

## Attempts to Explain Zn and Cd Performance, Using the Conventional Theory

Several approaches are made toward an explanation which would do least violence to the conventional theory.

These approaches depend in one form or another on the formation of reaction product of the Zn stabilizer, ($ZnCl_2$ or $HZnCl_2$) which catalyzes degradation of the vinyl. It is important to note that catalysis refers only to reaction rate. Since totally degraded PVC, such as Marvel, Sample and Roy (1939) obtained by prolonged treatment with KOH, is only red-brown, the black color of Zn product must imply a different reaction end-product.

### Effect of Oxygenated Groups on Color

It is essential to note that carbonyl groups can enter into conjugated double bond systems, and that their effect on the shift of the wave length of light absorption maxima is much greater than that of an additional olefin group.

A few examples from common experience will illustrate the point.

Naphthalene has, effectively, five conjugated carbon-to-carbon double bonds in its ring system. Yet it is colorless. Quinone has, effectively, four conjugated double bonds, of which two are of the C = O type and two of the C = C type. It is yellow. To attain a corresponding yellowness with C = C bonds in the absence of carbonyl group requires about 10 such conjugated links (using xanthophyll as an example). Thus, each C = O group is about as effective as 4 C = C groups is shifting the absorption wavelength.

The typical absorption maxima for olefinic bonds increase in wave length as more olefinic bonds are added in conjugation. Conjugated trienes absorb heavily in the 270-280 mμ range, which is also a characteristic absorption band for carbonyl groups. Here we equate one carbonyl group to 3 conjugated olefinic groups which is in fair agreement with our earlier example.

Some data on the extinction coefficients of systems involving conjugation of carbonyl groups with multiple olefinic linkages, suggest that the effect of the carbonyl group on intensity of color may be even more remarkable than its effect on the characteristic wave length of the absorbed light.

Druesdow & Gibbs (1953) suggested a cross-linking mechanism which would effectively limit the number of conjugated olefinic links to be expected in degraded vinyl. This would presumably give a reddish colored product. Winkler suggested that the resonance effect of polyenes which would tend to limit chain length by limiting the allylic degradation mechanism. If the conjugated system included carbonyl groups, however, even chains thus limited in length could presumably attain more intense and darker colors than the red of substantially non-oxygenated systems.

We, therefore, postulate a much higher degree of carbonyl participation in black completely degraded polyvinyl chloride systems; e.g., Zn- and Cd-containing systems, and, perhaps, some of the Sn-containing systems.

### The Origin of Carbonyl Groups in Degraded Vinyls

It is now necessary to develop a mechanism to explain the presence of high concentrations of carbonyl groups. The mechanics of oxidation of polymers with molecular oxygen is probably a free radical mechanism. It certainly appears to be so in polymeric hydrocarbons, and many of the discoveries in that field seem applicable to vinyls, too.

Assume that in our system, free radicals come into existence. For the moment, we shall not ask how. But, given these free radicals, we may proceed with a delineation of the oxidation phenomenon.

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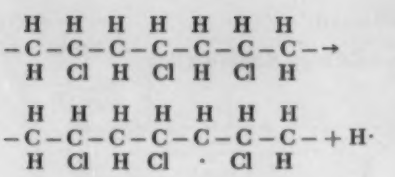

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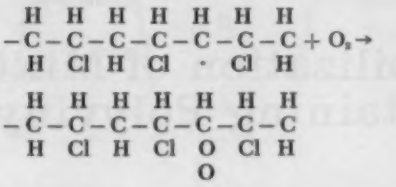

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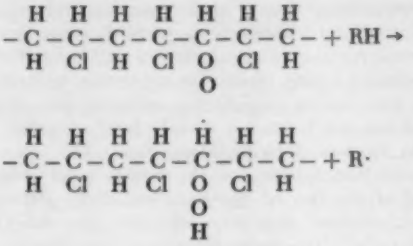

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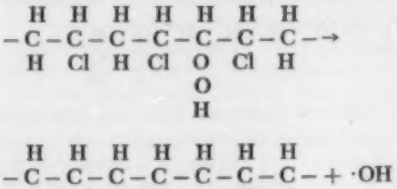

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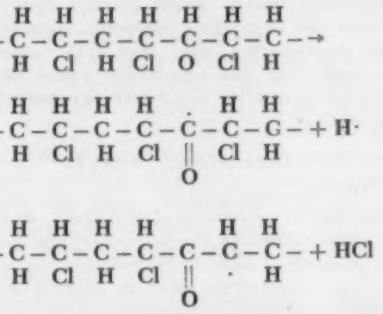

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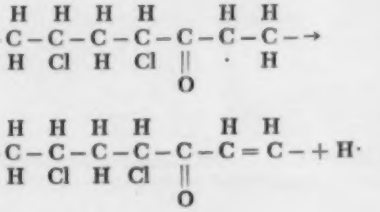
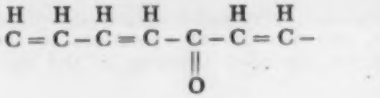


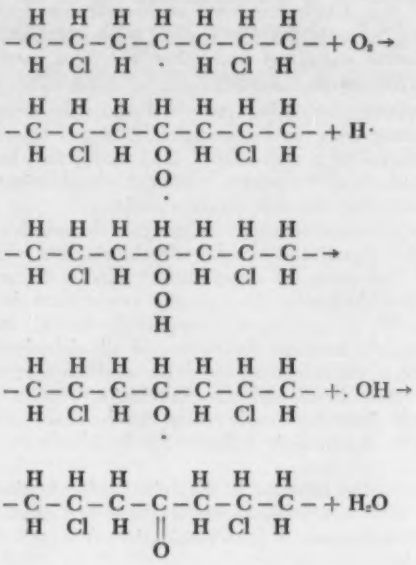
Which may easily progress to:



It is clear that such free radical dehydrochlorination is not the only type of free radical degradation. But, unlike those mechanisms which postulate chain scission with the formation of a terminal carbonyl group, the mechanism presented here offers a possible explanation for long conjugated systems by oxidation and dehydrochlorination.

The combination of H· radicals would result in the formation of $H_2$; while the combination of H· with ·OH would form water. Both of these products of vinyl degradation were observed by Achhammer.

A similar mechanism is possible for the degradation of a free radical formed by loss of a chlorine atom.



The carbonyl so placed between methylene groups appears less likely to induce conjugated double bond structure, although something approaching an allylic effect can be presumed from a keto-enol tautomeric shift affecting the carbonyl group.

But, here the conjugation is between carbon-to-carbon bonds only, and any reversion to the carbonyl configuration destroys the conjugation.

Nevertheless the carbonyl group formed in this manner are important. For the conjugated system formed by the first mechanism (based on the loss of a hydrogen atom) cannot by simple dehydrochlorination, or by repetition at the site of another methylenic H, create a conjugated system involving more than one carbonyl group.

If we continue to suspect that the black color formed in highly degraded Zn and Cd stabilized compounds is due to the presence of a multiplicity of carbonyl groups in the conjugated system, then we may have to have about as many carbonyls in Cl replacement sites, as in H replacement sites.

Not all oxidation intensifies color. Druesdow and Gibbs (1953) observed a reduction in color of oxygenated specimens of degraded PVC (compared with control samples in nitrogen) at equivalent levels of dehydrochlorination, and they offered a mechanism of 1, 4 oxygen addition to double bonds, breaking conjugated sequences, as an explanation of the color difference.

## The Modes of Dehydrochlorination

It is suggested that the removal of a molecule of HCl from polyvinyl chloride is not accomplished by the simultaneous ejection of H and Cl atoms from that molecule. Rather, it is thought that these atoms come off in some sequence, separated by a finite time, $\Delta t$, necessary for the effect of the loss of the first atom to induce the loss of the second.

During this time, important things can happen, which, in effect, results in a choice in the location of the second atom to be lost.

There are a number of alternates among which the choice is made. But, these choices can be conveniently classified into two groups: those involving neighboring carbon atoms on the PVC molecule, so that dehydrochlorination results in a double bond structure; and those involving carbon atoms which are not neighboring, and which need not necessarily be on the same molecule, so that dehydrochlorination results in the formation of tertiary or quaternary carbon structures, without double bonds. If the carbon atoms are on adjacent PVC molecules, we could, of course, have crosslinking.

Now for convenience in differentiating between these two classes of dehydrochlorination, the double-bond forming process is designed as *para-dehydrochlorination*, using the Greek prefix to indicate that the reaction occurs along the molecule, and dehydrochlorination between non-adjacent carbons whether or not on the same molecule, is designated as *dia-dehydrochlorination* to indicate that the new link is formed athwart the axis of the molecule.

Now the essence of the new theory is that *para-dehydrochlorination* and *dia-dehydrochlorination* both occur in commercial PVC mixtures, but that the *relative* rates of these two reactions are altered by the various ingredients and especially by the stabilizers.

It is further proposed that Zn and Cd soaps or their reaction products are dia-directing substances; that is, in their presence there is an increase in the ratio of dia-dehydrochlorination reactions to para-dehydrochlorination reactions.

## The Reduction of Olefinic Bonding by Zn and Cd Stabilizers

The production of tertiary and quaternary carbons has not only the negative value of not producing per se any double bonds, but it has the additional value of providing limits to the length of the conjugated double bond systems. Thus, the Zn and Cd soaps, by virtue of their postulated dia-directing character would reduce early discoloration.

## The Origin of Free Radicals in Zn and Cd Stabilized Systems

Large molecules, in systems under thermal or mechanical strain, depend for their structural stability on their ability to deform easily. This deformation is easily accomplished in a system in which free rotation is possible among the linearly arranged carbon-to-carbon bonds.

But as cross-links are formed, the system loses its loose-chain freedom. Random molecular impacts which increase in violence as the temperature rises begin to develop considerable internal stresses. One may imagine perhaps a very long freight train with engines at each end racing forward, stopping and reversing themselves in some uncoordinated fashion. We would agree that between the "humpings" and the sudden tensile stresses at the couplings, the wear and tear on the train would be considerable. Now extend this idea to two such trains on neighboring tracks with occasional tight steel bands joining cars from the neighboring trains. It is clear that very soon these steel bands would snap, or if they were strong enough, they would wrench car after car from the rails and wreck the train.

Now regard the steel bands as the molecular cross-links. Their snapping would correspond to the sudden creation of two free radicals. We have already indicated some mechan-

isms by which such free radicals may undergo oxidative degradation.

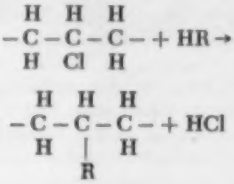
### Variations in Dia-dehydrochlorination

Examine further some of the variants of this proposed dia-dehydrochlorination. In a typical vinyl formulation, the Cl atom must come from the PVC molecule (I exclude from consideration at this time systems containing other chlorinated additives). The H atom may come from the same PVC molecule, from another PVC molecule, from the plasticizer, from the stabilizer, or from the filler.

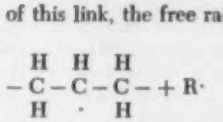
Of these, some general forms of classification may be useful as follows:

Consider all these substances prior to dia-dehydrochlorination as represented by the formula RH.

The reaction then proceeds:

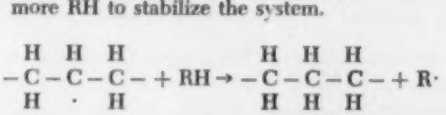


Now on rupture of this link, the free radicals are formed:



If R· is relatively stable, then the situation is innocuous for the following reasons:

1. There is only one active free radical instead of two.
2. The active free radical can readily recombine with more RH to stabilize the system.



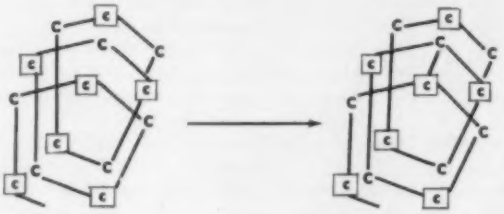
R· can, however, represent a wide range of stability. The discussion of the stability of particular free radicals is, however, outside the scope of this report.

### Intramolecular Dia-dehydrochlorination

An important special case, however, is dia-dehydrochlorination involving the same PVC molecule.

While the PVC molecule is substantially linear, it is not straight. Free rotation of the C – C bonds permits a variety of configurations. It should be very easy for the PVC molecule to coil on itself. The bond angles are such that a spiral formation with five carbons per coil would not involve any appreciable strain. In fact, an added stability would obtain since the chlorine-bearing carbons would alternate with methylenic carbon as we proceed from coil to coil along a line paralleling the axis. There is thus excellent opportunity for dia-dehydrochlorination to form a six-membered ring. As would be expected, such a ring would not be in one plane, being related to cyclohexane.

The carbons in the squares are the carbons of the methylene groups; the others, of –CHCl– groups. The reaction illustrated shows an intramolecular crosslink.



Cleavage of the ring at the site of the dehydrochlorination would result in two free radicals, so situated that on oxidation and dehydrochlorination, two carbonyl groups plus associated olefinic linkages would all be in conjugation.

This pattern would thus lead to intense discoloration.

The suggestion of such coiling of molecules is reminiscent of Doty's work on the coiling of some polypeptide molecules in solution. Polypeptide coiling is a much more complex phenomenon than that suggested here, but the analogy exists.

### Generalization of the Theory

So far, this article has been concerned principally with Zn– and Cd– stabilized systems. It is possible however, to include other stabilizers and other stabilizer mechanisms, and to arrive at the following general theory:

a. Mixtures containing polyvinyl chloride degrade on heating with the evolution of hydrogen chloride.
b. Removal of a molecule of HCl may result in olefinic double bond formation (para-dehydrochlorination); or it may not (dia-dehydrochlorination).
c. The presence of additives modifies the relative ratio at which para- and dia-dehydrochlorination occur. Zn, Cd and some Sn compounds probably favor dia-dehydrochlorination, to a greater extent than do Ba, Pb, Na, Sr, Ca and epoxy compounds, but all stabilizers probably increase the degree of dia-dehydrochlorination, when compared with the stabilizer-free polymer.
d. Increase in dia-dehydrochlorination results in relatively improved early color in thermally degrading vinyls, because it reduces the buildup rate of long chain polyenes.
e. Substantial increase in dia-dehydrochlorination results in more darkly discolored products of ultimate degradation because it favors oxidative, free-radical degradation.
f. The improvement of the color of systems favoring para-dehydrochlorination can be accomplished principally by adding stabilizer which favor dia-dehydrochlorination to interrupt the polyene sequences, or by adding compounds which add to polyenes or split them.
g. The improvement of the performance of systems favoring dia-dehydrochlorination can be accomplished by adding para-directing substances which reduce, by competition with dia-directing substances, the number of sites of probable initiation of free-radical chain reactions, and which by introducing olefinic double bonds reduce the flexibility of the PVC molecule and thus reduce coiling; and by the addition of substances capable of stopping or moderating the rate of free-radical reactions.

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# Creep Behavior of Transparent Plastics at Elevated Temperatures

*This article gives results of experiments designed to measure creep elongation of plastics exposed to temperature differentials and biaxial stresses. The article points the way towards defining temperature limitations for plastics being considered or now used as aircraft glazing such as canopies.*

Many materials exhibit creep, or change in shape or dimension, under protracted loading. Creep is a function of stress, time, and temperature; i.e., the amount of stress that is applied, the length of time it is applied, and the temperature of the material.

Plastics are susceptible to creep, especially in structural applications where they must withstand large stresses and, frequently, high temperatures. This investigation of the creep behavior of transparent plastics was undertaken to define the upper temperature capabilities of plastics used and considered for use as aircraft glazing such as canopies, windows, and windshields. In such applications the creep behavior is an important consideration in the choice of the plastic and in aircraft canopy design, especially when the glazing must withstand high temperatures developed by air friction.

The simplest method for measuring the creep behavior of a material is to apply a constant load to a strip of the material at a constant temperature and measure the resulting elongation as a function of time. The strip of material may be enclosed in a furnace for measurements at high temperatures. Thus, the material is exposed to uniform temperatures and uniaxial stress.

However, the conditions under which plastics are used are often not adequately simulated by the simple creep test. For example, aerodynamic heating of aircraft glazing materials results in large temperature differentials between the heated outer surface and the cooled inner surface of the glazing. Under this temperature differential the glazing may withstand considerably higher temperatures on its outer surface without excessive creep elongation than if the material were heated uniformly to the outer surface temperature. Also, the simple creep test subjects the plastic to uniaxial stress, but plastics in the form of sheets are generally subjected to biaxial stresses in use. Therefore, experiments were designed to measure the creep elongations of plastics exposed to temperature differentials and to biaxial stresses. Ultimately both investigations will be combined to better simulate actual service conditions for aircraft glazing.

The first part of this paper reports the results of simple creep elongation measurements for a number of transparent plastics. The temperature-differential studies and the biaxial-stress studies are discussed separately after the simple creep results.

Details of the equipment and procedures used for the studies of simple creep and creep under a temperature differential have been described by Slone and Reinhart (Ref. 1). The data for the heat-resistant and modified acrylics reported by them are included in this paper for comparative purposes.

## Simple Creep

The creep elongations of five different transparent plastics were measured at uniform temperatures under unaixial stress in order to compare the materials and to study the effects of time, temperature, and stress on the creep elongations. The information obtained was useful also in simplifying the evaluation of the more complex temperature-differential and biaxial-stress studies. The plastics studied are listed in Table I.

Fig. 1 shows the elongation of heat-resistant polymethyl methacrylate as a function of time at various stresses. The temperature was constant at 190°F. Fig. 2 shows the elongation of the same material as a function of time at various temperatures. The stress was constant at 1000 psi. The elongations in these and the succeeding figures include the elastic and viscoelastic elongations but do not include the elongation due to thermal expansion.

The above figures show that creep elongation is not a linear function of time but, in the range of these experi-

**Materials Investigated**

| | Thickness in. |
|---|---|
| General-Purpose Acrylic | 0.375 |
| Heat-Resistant Polymethyl methylacrylate | 0.375 |
| Modified Acrylic | 0.395 |
| Polyester I | 0.375 |
| Polyester II (more recently developed than I) | 0.25 |

[1] This work was sponsored by the Airborne Equipment Division, Bureau of Aeronautics, Department of the Navy, under Contract Projects NBS AE 4400 and 4403.

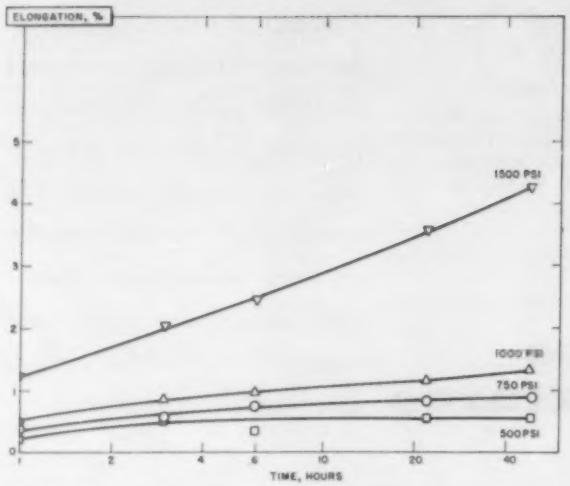


**Figure 1.** Creep of heat-resistant polymethyl methacrylate at 190°F.

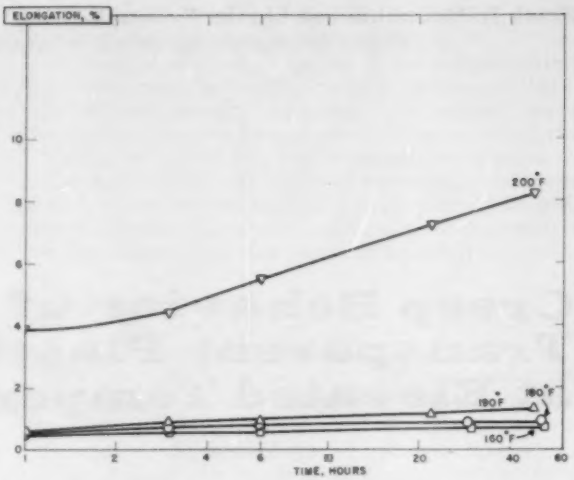


**Figure 2.** Creep of heat-resistant polymethyl methacrylate under 1000 PSI stress.

ments, is nearly linear with the logarithm of time. Fig. 2 also shows that the relationship between elongation and temperature is nonlinear.

While the above figures are useful to study the effects of the different variables, it is more convenient to compare the different materials in curves of stress versus elongation after 50 hours, at different temperatures. Figs. 3 through 7 are such curves for the materials listed in Table I. The axes of all the figures are drawn to the same scale, but it should be noted that the test temperatures were varied for different materials. These figures show that the creep elongation after 50 hours does not vary linearly with the applied stress.

The general-purpose acrylic plastic was the least temperature-resistant of the materials investigated. A stress of 1000 psi at 160°F resulted in rapid elongation and specimens subjected to a stress of 1500 psi at 160°F broke in from 3 to 7 hours. The associated elongations were over 13%.

The heat-resistant polymethyl methacrylate elongated less than two percent below 180°F, but showed appreciable creep under stresses of 1000 psi and higher at temperatures of 190°F and higher. The curve for 200°F in Fig. 4 is uncertain because the results obtained at the different stresses were erratic.

The modified acrylic showed little elongation at 190°F and below and had only 4% elongation at 1500 psi at 200°F.

The creep behavior of polyester I was quite different from that of the acrylics. At 160°, 180° and 190°F, the elongation of polyester I was more than double that of the heat-resistant polymethyl methacrylate at all of the applied stresses. But at 200°F the situation changed; the elongation of polyester I specimens under a stress of 500 psi was about the same as for the acrylic specimens at 500 psi, and at 750 psi the elongation of the polyester I was much less than that of the acrylic plastic. However, the total elongation of the polyester specimens was limited; fracture occurred at about 4½% elongation. For example, polyester I specimens under a stress of 1500 psi at 180°F broke in less than 10 hours and at the same stress at 190°F polyester I specimens broke in from 1 to 2 hours. At 200°F, polyester I specimens under a stress of only 1000 psi broke in several hours. The fractures of the polyester I specimens

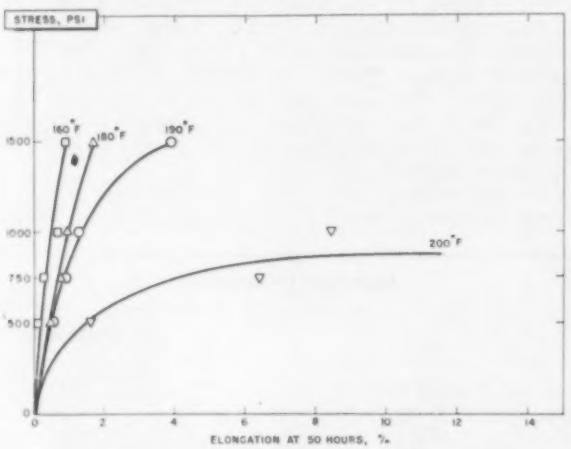


**Figure 3.** Creep elongation of general-purpose acrylic plastic at 50 hours after stress is applied.

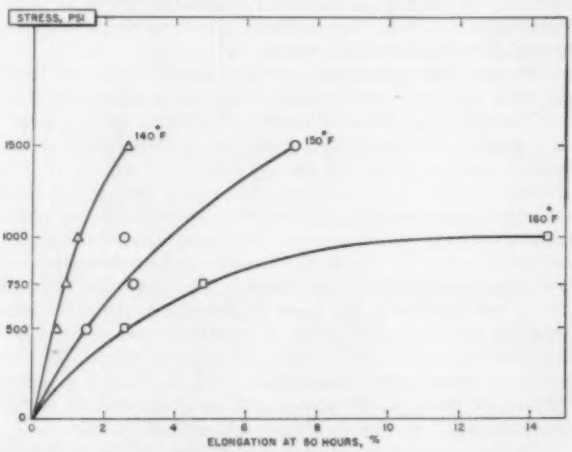


**Figure 4.** Creep elongations of heat-resistant polymethyl methacrylate at 50 hours after stress is applied.

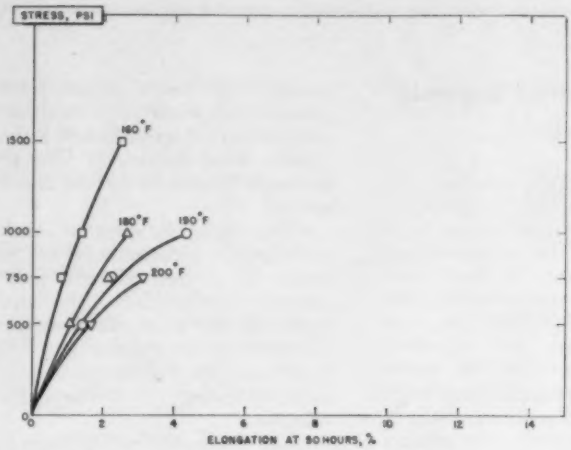


**Figure 5.** Creep elongations of modified acrylic plastic at 50 hours after stress is applied.

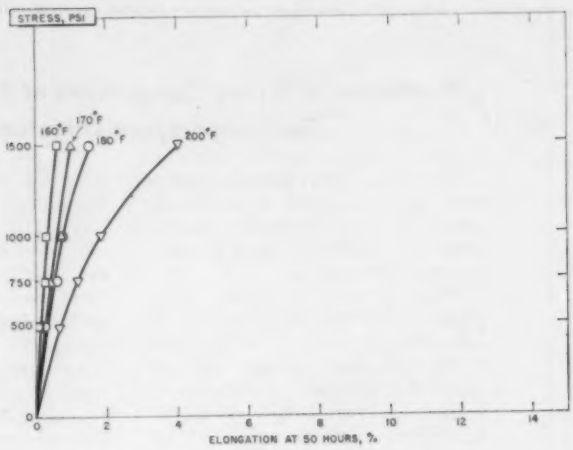


**Figure 6.** Creep elongations of polyester I at 50 hours after stress is applied.

were clean; there was no evidence of necking down as with the acrylics.

Polyester II was the most temperature-resistant material studied. Though it showed a rather high elongation of 3¼% at 240°F under a stress of 1500 psi, this elongation did not increase rapidly with temperature in comparison with the other materials.

Fig. 8 is a bar graph for quick comparison between the materials studied. It indicates the estimated temperature necessary for a material to develop an elongation of 2% and 4% while sustaining a stress of 1000 psi for 50 hours. The elongations chosen for this comparison represent approximately the maximum creep allowed for many applications of the plastics. An elongation of 2%, the usual limit for aircraft glazing, is equivalent to ¼" extension for each foot of length, and 4% to ½" extension for each foot. The temperatures indicated appear to be rather critical for each material since a small increase in temperature doubles the creep elongation.

### Temperature Differential Studies

Since some uses of plastics involve non-uniform temperature conditions, the creep elongation of a specimen exposed to different temperatures on opposite faces was investigated. Typical results are shown in Figs. 9 to 13 by solid lines.

The creep elongations of specimens exposed to temperature differentials were always much less than the elongations of specimens exposed to a uniform temperature equal to the hot-face temperature. Therefore, the creep elongations of specimens exposed to temperature differentials were compared with creep elongations of specimens exposed to uniform temperatures equal to the mean temperature, which is defined as the average of the temperatures of the two faces of the specimen exposed to a temperature differential.

The creep elongations for specimens at a uniform temperature equal to the mean temperature are shown in Figs. 9 to 13 by dotted lines. Also, creep elongations calculated by a theory given in Appendix A are shown by dashed lines in these figures.

The creep elongations for the heat-resistant and modified acrylic plastics exposed to temperature differentials were generally less than or equal to their elongations when subjected to a uniform temperature corresponding to the mean temperature of the temperature-differential test. The one exception, shown in Fig. 12, was the modified acrylic

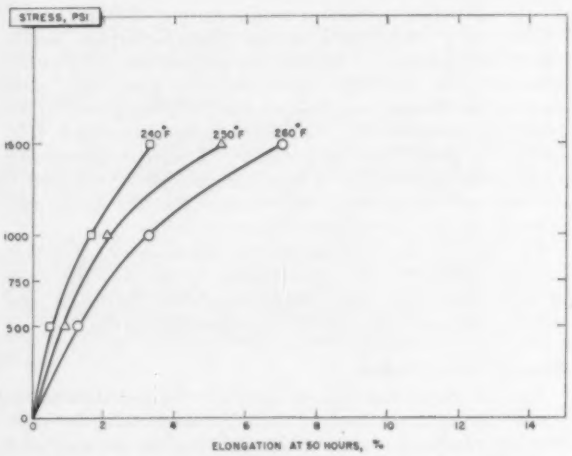


**Figure 7.** Creep elongations of polyester II at 50 hours after stress is applied.

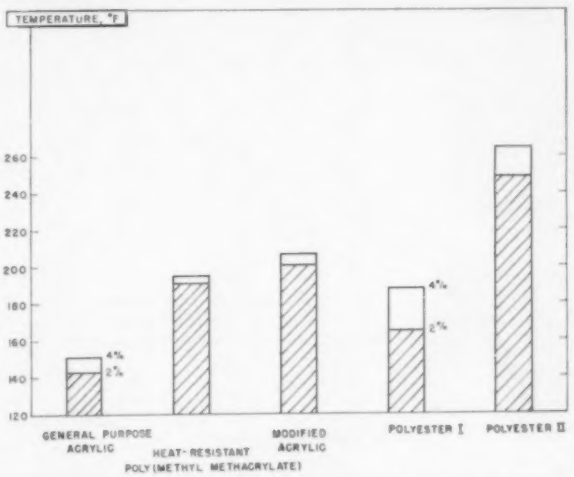


**Figure 8.** Estimated temperatures to produce creep elongations of 2% and 4% at 50 hours after a stress of 1000 PSI is applied.

## Prediction of Creep Elongations of Plastics Exposed To Temperature Differentials

The data from simple creep tests may be used to calculate curves of creep elongation versus stress for plastics exposed to temperature differentials.

When a load is applied to a plastic strip specimen heated to different temperatures on opposite faces, the stress is not uniform across the specimen, but decreases continuously from the rigid cooler face to the less rigid hot face. The distribution of local stresses averaged across the specimen must equal the applied stress.

The local stress at a point in the specimen is a function of the temperature and the creep elongation at the point. Since the temperature gradient across the specimen is approximately uniform (Ref. 2), the temperature at any point in the specimen is easily determined. The creep elongation can be calculated for an assumed total elongation of the specimen as shown below. The creep elongation includes both the elastic and viscoelastic components.

The total elongation at any point in the specimen is the sum of the thermal expansion and creep elongation and is constant throughout the specimen. However, since the temperature varies across the specimen, the thermal expansion and, therefore, the creep elongation will vary. The thermal expansion at any point may be calculated from the temperature at that point. Then, for an assumed total elongation of the specimen, the creep elongation may be calculated. Since the length of the heated specimen is used as the base length for elongation measurements, the thermal expansions (or contractions) are referred to the mean temperature of the specimen rather than to the specimen temperature before the specimen was heated.

After the creep elongation at a point has been calculated for an assumed total elongation, the stress necessary to produce that creep elongation may be found from simple creep data at the same conditions of time, temperature and elongation. By determining the local stress at each of several points across the specimen and averaging the local stress distribution, the average stress necessary to produce the assumed elongation of the specimen is calculated. The local stress distribution is assumed to be independent of time.

A curve of creep elongation versus stress can be obtained for specimens exposed to a temperature differential by calculating the average stress for several different assumed elongations by the above method.

For example, the stress necessary to cause 1% elongation after 50 hours in a heat-resistant polymethyl methacrylate specimen heated to 250°F on one face and to 150°F on the opposite face will be determined. Fig. A-1 is a schematic drawing to illustrate the solution.

Since the coefficient of thermal

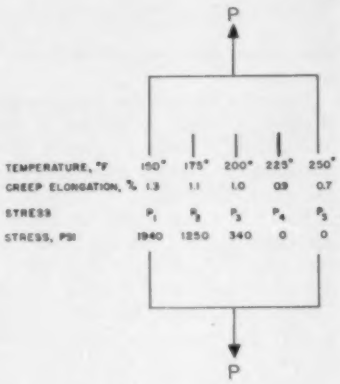


**Figure A-1.** Schematic drawing of a creep test of heat-resistant polymethyl methacrylate exposed to a temperature differential.

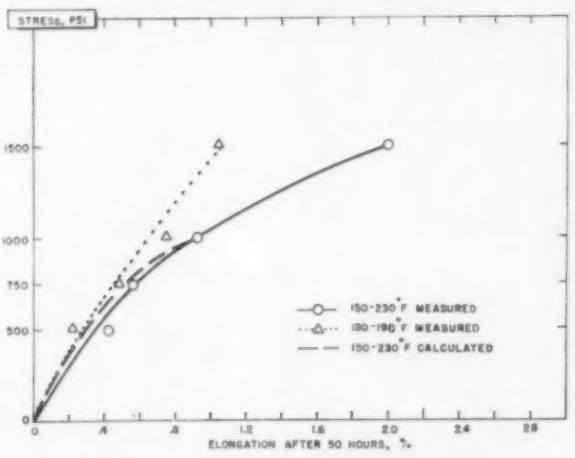


**Figure 9.** Creep elongations at 50 hours after stress is applied to heat-resistant polymethyl methacrylate exposed to a temperature differential and to a uniform temperature. The mean temperature is 190°F.

plastic exposed to 150° and 250°F on its surfaces, where the creep elongations were significantly larger than for the plastic exposed to a uniform temperature of 200°F.

The creep elongations of the general-purpose acrylic plastic and polyester I exposed to temperature differentials were generally less than those observed when they were exposed to the uniform temperature corresponding to the mean temperatures of the temperature-differential tests. The creep elongations of polyester II were approximately equal when exposed to a temperature differential and to the uniform temperature corresponding to the mean temperature of the temperature-differential tests.

The dashed curves calculated by the theory of Appendix A agree well with the experimental values over the range of stress for which the calculations could be made, considering the variability of the experimental values.

### Biaxial Stress Studies

Fig. 14 shows the type of specimen subjected to biaxial stress. During a test, each of the 12 projections of the specimen are placed in clamps and equal tensions are applied to each projection. These tensions produce a uniform biaxial stress condition in the center of the specimen, although the sides of the specimen near the projections are subjected to

expansion for heat-resistant polymethyl methacrylate is about 5.5 x $10^{-5}$ in/in. °F at 200°F, the hot face will expand 5.5 x $10^{-3}$ (250-200), or 0.3%, and the creep elongation at the hot face will be 1-0.3, or 0.7%. This creep elongation and others calculated the same way are shown in Fig. A-1. The local stresses, $P_1$ to $P_5$, necessary at each point to obtain the indicated elongation, were obtained from Fig. 4, directly or by extrapolation. They are also shown in Fig. A-1.

The average stress, P, to be applied, is found by averaging the local stress distribution. Using Simpson's rule (Ref. 3) of numerical integration gives

$$P=(P_1+4P_2+2P_3+4P_4+P_5)/12.$$

In this example the average stress, P, is calculated to be 625 psi.

The dashed curve in Fig. 10 was obtained by repeating the above calculation for several other assumed elongations, and the calculated curves in Figs. 9, 11, 12, and 13 were found in the same manner.

## Creep of Plastics Subjected to Biaxial Stress

The creep behavior of plastics subjected to biaxial stress is derived from the analogous elastic problem. The unit elongation of an elastic sheet subjected to equal biaxial stresses is (Ref. 4)

$$e_b = P(1-\mu)/E$$

where P is the stress, $\mu$ is Poisson's ratio, and E is Young's modulus. Poisson's ratio is eliminated from this equation by use of the bulk modulus (Ref. 4)

$$K = \frac{E}{3(1-2\mu)}$$

to give

$$e_b = 1/2\,P/E + P/(6K)$$

For a specimen subjected to uniaxial stress P, the unit elongation is $e_u = P/E$.

Therefore,

$$e_b = 1/2\,e_u + P/(6K).$$

for an elastic sheet.

By analysis of Alfrey and Gurnee (Ref. 5), the solution for the elastic sheet is valid for the creep behavior of a linear viscoelastic sheet if the elongations and moduli are replaced by creep elongations and creep moduli which are functions of time. For the theory of creep of plastics under biaxial stress, linear viscoelastic behavior of the plastics is assumed. Therefore, neglecting the time-dependence of the bulk modulus, K, the creep elongation of a plastic specimen subjected to biaxial stress is

$$e_b(t) = 1/2\,e_u(t) + P/(6K).$$

Sharp and Maxwell (Ref. 6) give values of 4.3 x $10^5$ and 1.59 x $10^5$ psi for Young's modulus, E, and shear modulus, G, respectively, of polymethyl methacrylate at 30°C. Calculation of K by the formula (Ref. 7)

$$K = \frac{EG}{3(3G-E)}$$

gives 4.85 x $10^5$ psi. Since the bulk modulus is not expected to be very sensitive to temperature (Ref. 8) or modifications of polymethyl methacrylate, this value of the bulk modulus may be used as an approximation for the high temperature conditions considered in this paper.

For a stress, P, of 1000 psi

$$P/(6K) = 3 \times 10^{-4} = 0.03\%.$$

Thus P/(6K) is small under the conditions of interest, so that approximately $e_b(t) = 1/2\,e_u(t)$. This result depends upon the stress being small, that is, of the order of 1000 psi. For larger stresses the term P/(6K) must be included.

The assumption of linear viscoelasticity is a serious limitation of this theory, since Figs. 3 to 7 show that the creep elongations of the plastics investigated do not vary linearly with the applied stress. However, as a first approximation the curves in Figs. 3 to 7 may be considered as straight lines and linear viscoelasticity may be assumed.

non-uniform stress conditions. The temperature of the specimen is controlled by ovens that fit around the specimen.

The distances between the intersections of the lines drawn on the specimen are measured by a cathetometer during a test. From these distances the creep elongation of the specimen is calculated.

Only a few biaxial stress creep tests have been performed to date. These tests showed that the creep elongations under equal biaxial stresses were only about one-half of the creep elongations of the materials subjected to uniaxial stress.

A theory of creep behavior of plastics subjected to biaxial stress is given in Appendix B. This theory predicts that the creep elongation of a plastic subjected to biaxial stress is about half the creep elongation of the plastic subjected to uniaxial stress, in agreement with the experimental results.

## Conclusions

The creep behavior at elevated temperatures of three acrylic and two polyester plastics was measured. Polyester II was the most creep-resistant and general-purpose acrylic plastic was the least creep-resistant of these plastics at elevated temperatures.

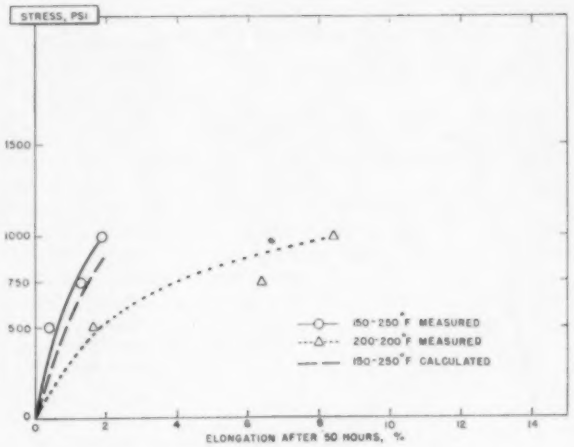


**Figure 10.** Creep elongations at 50 hours after stress is applied to heat-resistant polymethyl methacrylate exposed to a temperature differential and to a uniform temperature. The mean temperature is 200°F.

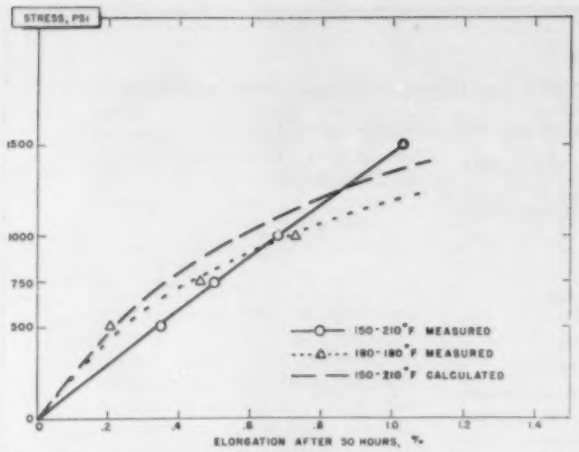


**Figure 11.** Creep elongations at 50 hours after stress is applied to modified acrylic plastic exposed to a temperature differential and to a uniform temperature. The mean temperature is 180°F.

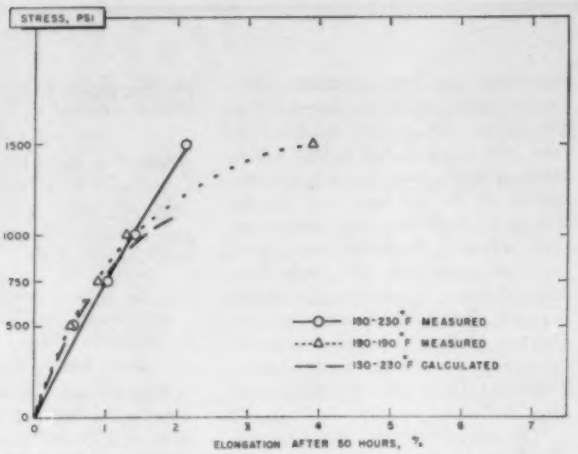


**Figure 12.** Creep elongations at 50 hours after stress is applied to modified acrylic plastic exposed to a temperature differential and to a uniform temperature. The mean temperature is 190°F.

The measured creep elongations did not vary linearly with either the length of time that stress was applied, the applied stress, or the temperature of the specimen. The elongations increased rapidly with temperature, especially for the acrylics at the higher temperatures. The creep elongations for the plastics exposed to temperature differentials were generally less than or equal to their elongations when they were exposed to the uniform temperature corresponding to the mean temperatures of the temperature-differential tests. A theory of creep of a plastic exposed to a temperature differential was shown to agree with the measured elongations.

Creep elongations of specimens subjected to equal biaxial stresses were found to be less than the corresponding elongations of specimens subjected to uniaxial stress. Approximate agreement with a theory of creep under biaxial stress was obtained.


### Acknowledgments

The creep measurements of general-purpose acrylic plastics were made by Leon Horn and Catherine Simpson and the measurements of heat-resistant and modified acrylics were made by Murray C. Slone.


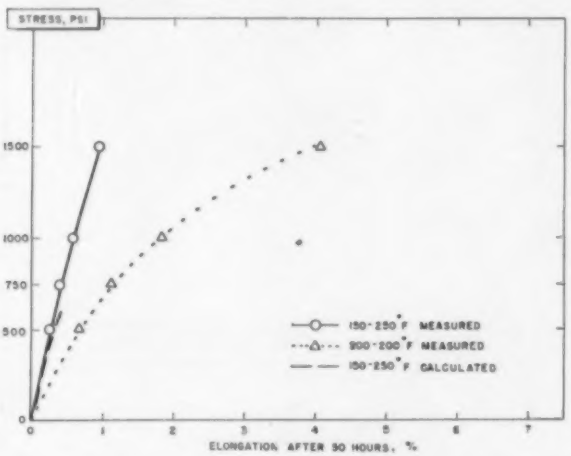


**Figure 13.** Creep elongations at 50 hours after stress is applied to modified acrylic plastic exposed to a temperature differential and to a uniform temperature. The mean temperature is 200°F.

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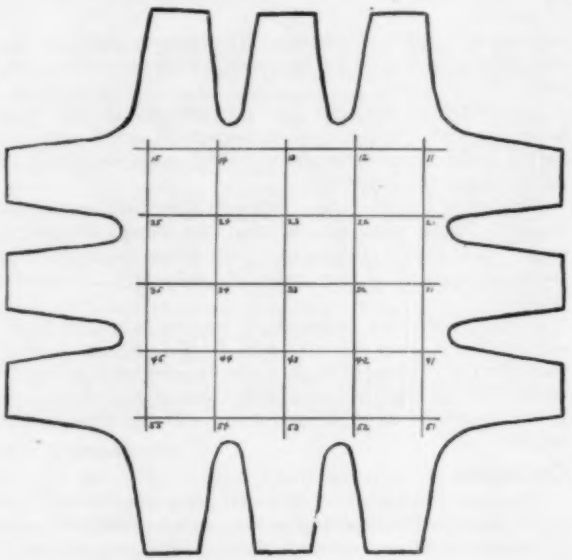

**Figure 14.** Specimen for biaxial stress tests.

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# Infrared Spectra and the Structure of High Polymers

Polymer Science

**Edited by: Irvin Wolock**
*U.S. Naval Research Laboratory*

The use of infrared spectroscopy as an analytical tool for the study of complicated molecular systems is widely appreciated. The fact that small groups of atoms (such as $CH_2$, OH, C = O, etc.) undergo internuclear vibrations whose frequency is essentially independent of the size and complexity of the molecule in which they are located has led to the use of the infrared spectrum as a simple and rapid method for detecting the presence of such groups. Since each molecule is a unique combination of such groups, it is furthermore often possible to make use of the infrared absorption spectrum as a means of detecting a particular molecular species, the spectrum acting, so to speak, as a "finger-print" of the molecule. These simple facts account for the tremendous potentialities of this technique, both as a qualitative and as a quantitative analytical method.

Until recently, a discussion of the infrared spectra of high polymers would have begun in this vein and proceeded by illustrating the various ways in which such group frequencies have been used. This could be anything from determining the nature of the chemical changes on oxidation of a polymer to estimating the percent of vinyl unsaturation in a given polymerizate to evaluating the extent of crystallite orientation in a stretched polymer film. As a result of developments in recent years, it is possible now to meaningfully shift the emphasis of such a discussion to two very basic aspects of infrared studies of polymers: first, the problem of a complete understanding of the spectrum of a polymer, and second, the question of information about the more detailed characteristics of the structure that is revealed by the spectrum. The advances which have taken place recently are related primarily to our ability to interpret more completely the spectrum of a polymer. As a result, however, it is now possible not only to increase the range of applications of the kind mentioned above, but to use the infrared spectrum as a tool for a more detailed insight into aspects of polymer structure. The importance of the latter development hardly needs to be emphasized in view of the manner in which our knowledge of the structure of high polymers underlies our understanding of their physical properties, and in view of the fact that different techniques often provide non-overlapping kinds of structural information. The aims of the present discussion will be to describe the developments in our ability to interpret the infrared spectra of polymers, and to illustrate the type of structural information which has resulted from this enhanced understanding.

## Vibrational Spectral Analysis

Before discussing the spectral analysis of polymers, it is pertinent to review briefly the origins of vibrational spectra and their application to the study of small molecules (Refs. 7, 30). The general procedure which is followed in this analysis is to compare the observed spectrum with that predicted from theory. The extent of agreement is a measure of the confidence that can be placed in the assumptions as to structure and interatomic forces which have to be made in the theoretical analysis. As we shall see in the case of the polymer spectra, this is the manner in which structural information can be derived from spectral studies.

A system of N interconnected masses can vibrate, if given energy, in an infinite number of ways which differ from each other in the amplitude, frequency, and phase of motion of the individual masses. Yet each one of these vibrations can be constructed by superimposing, with appropriate relative amplitudes, a finite number (in general, 3N−6) of characteristic modes of oscillation. These are the normal modes of vibration, and they have the property that in a given mode all of the masses move with simple harmonic motion of the same frequency. The determination of these normal modes and their frequencies is a straightforward problem in classical mechanics. The procedure is of course applicable to molecular systems, and as an illustration of the results we show in Fig. 1 the normal modes of the $H_2O$ molecule.

These normal modes of vibration are of significance in three ways. First, their frequencies are a function of the structure and interatomic forces in the molecule. This means that if the modes can be identified and their frequencies determined experimentally, it becomes possible, by inverting the relationship so to speak, to obtain information on the structure and force field of the molecule. Second, these classical vibration frequencies are of direct relevance to the solution of the quantum mechanical energy problem. As we know, a molecular system can exist only in certain discrete states of electronic, vibrational, and rotational energy. In the present case we are interested only in the energy changes involving transitions between the quantized vibrational energy levels. The possible energies of these states are given by

$$E_i = h\nu_i(v_i + \frac{1}{2})$$
$$v_i = 0, 1, 2, \ldots \qquad \text{(Eq. 1)}$$

where $\nu_i$ is the classical oscillation frequency for the $i^{th}$ normal vibration. Thus, the solution of the classical vibration problem is also appropriate to the necessary quantum mechanical descripition of the molecular system. Third, since the normal modes are the only simple periodic motions of the nuclei in the molecule,

**Figure 1.** Normal modes of vibration of the $H_2O$ molecule.

the normal frequencies are the frequencies involved in interaction with the periodically varying electric field of a light wave. The nature of this interaction is the following: if there is a change in the dipole moment of the molecule during a particular normal vibration, then the molecule can absorb (infrared) radiation corresponding to that normal frequency; if there is a change in the polarizability of the molecule during the normal vibration, then Raman scattering can occur, i.e., the scattering of monochromatic visible light with a frequency change corresponding to the normal vibration frequency. From infrared and Raman spectra we can thus experimentally determine the normal vibration frequencies of a molecule.

The determination of the normal modes according to the procedure indicated above is often not an easy task, particularly in the case of a molecule with many atoms. This is because we not only need to know the force field of the molecule in order to do the calculation, but even after this is known the solution of a 3N x 3N determinantal equation is required, by no means a simple task for large molecules. Fortunately, there is an aspect of the structure which often leads to considerable simplification of the problem, viz., the symmetry properties of the molecule. If a molecule has symmetry, i.e., if when certain operations are performed (rotations, mirror reflections, etc.) the molecule is brought to a configuration indistinguishable from the original one, then it is possible to predict many aspects of its spectrum without any further knowledge about the molecule. These predictions include the number of normal modes possessing a given type of symmetry, their activity in the infrared and Raman spectra, possibilities of interaction, and so on. In addition, symmetry considerations permit a reduction in the order of the determinantal equation which must be solved, thus easing the computational aspects of the problem.

In spite of these simplifications, a detailed theoretical analysis is usually a very formidable problem for any but the simplest molecules. If not for the existence (to first approximation) of the group frequencies mentioned earlier, infrared spectroscopy would be far less powerful an analytic technique for the study of complex molecules than it actually is. Group frequencies arise because of the relative constancy of bond force constants from one molecule to another, and because groups which involve light atoms (such as hydrogen) or strong bonds (such as C=C) tend to have normal vibrations which do not depend strongly on the nature of the remainder of the molecule. As a result we expect certain of the normal modes of the molecule to consist of internuclear vibrations which are essentially localized in the group, and therefore the frequencies of this group will be approximately the same from molecule to molecule. For example, all molecules containing $CH_2$ groups exhibit absorption bands in the range of roughly 2850 to 2950 $cm^{-1}$*. Correlations of characteristic frequency ranges with specific groups have been investigated in great detail (Ref. 1), and furnish a good first approximation to the spectral location of normal modes of this type. In higher approximation we do not expect these group modes to be independent of their environment; in fact we would anticipate that the small variations in frequency which occur from one molecule to another should provide a clue (if they can be interpreted) to the nature of the interaction between the group and its environment. These considerations, plus the fact that some of the normal modes cannot be localized but involve significant motions of many of the atoms in the molecule, require that the group frequency concept be used with caution when a complete interpretation of a spectrum is required.

* Absorption bands will be characterized by their frequency in $cm^{-1}$ (waves per cm.), where this frequency is given by $10^4/\lambda$, $\lambda$ being the wavelength in microns.

## Spectral Analysis of Macromolecules

Until recently, the study of the spectra of high polymers was based primarily on the group frequency analysis of some of the observed absorption bands. The primary shift of emphasis in recent work has been toward an attempt to obtain a complete interpretation of the spectrum, i.e., to determine and assign all of the normal vibrations (group and otherwise) of the molecule. This is understandably a more difficult and extended task, and has been achieved with varying degrees of success for different polymers. The argument of this article is to show that it is potentially a more powerful approach, one which may well reward the additional effort involved. The basic aspects of this analysis, both the theoretical and the experimental, will now be considered in somewhat greater detail.

*Theoretical.* As pointed out above, a spectrum is analyzed in terms of theoretical predictions based on an assumed model. The extent of agreement between observed and predicted results is a measure of the validity of the assumed structure and internal force field. We will consider, in terms of specific examples, the two main aspects of the theoretical analysis, viz., symmetry classification of normal modes and the computation of normal frequencies.

It was mentioned above that knowledge of the symmetry of a molecule alone can furnish much information about its spectrum. This has proven to be most useful in the analysis of polymer spectra. Consider the case of a single, infinitely long, extended polyethylene chain, shown schematically in Fig. 2 with its associated symmetry elements. It is a one-dimensionally periodic structure which is identically reproduced by any of its symmetry operations, e.g., the rotation of 180° about the x-axis followed by a translation of half the repeat distance along this direction (the $C_2^*$ operation). This set of symmetry operations forms a group (in the mathematical sense), to which can be applied the results of group theory (Refs. 11, 20, 28). We are not concerned here with the methods of group theory but with the result, which is given by what is called a character table. The character table for a single polyethylene chain is shown in Table I. It tells us that the normal modes are grouped into symmetry species (designated $A_g$, $B_{1g}$, etc.), the motions of the nuclei in a normal mode under a given species having the symmetry properties of that species ($1 \equiv$ symmetric, $-1 \equiv$ antisymmetric). Thus, all modes of symmetry $B_{2g}$ are symmetric with respect to the identity operation (E), antisymmetric with respect to the twofold rotation axis along z, symmetric with respect to the twofold rotation axis along y, etc. Furthermore, the symmetry analysis provides the total number ($n_i$) of normal modes belonging to each species, and also breaks these down into translations (T) of the chain as well as translatory (T'), rotatory (R'), and internal ($n_i'$) modes of the two $CH_2$ groups in the structural repeat unit. With the help of this information it is possible to surmise the symmetry modes, i.e., those vibrations which satisfy the symmetry characteristics of a given species. The normal modes within a given symmetry species are combinations of the symmetry modes within that species alone, and are often quite close to the symmetry modes themselves. Such modes for the polyethy-

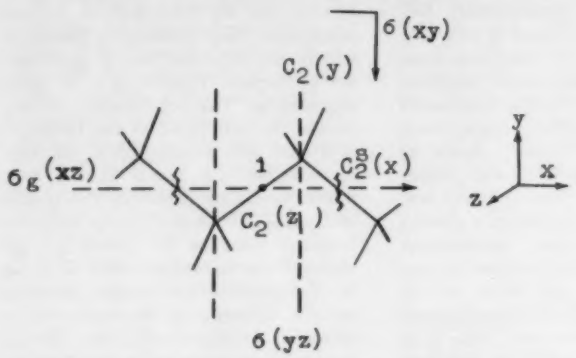


**Figure 2.** Polyethylene chain and symmetry elements: $C_s$ - diad, $C_2^s$ -screw diad, $\sigma$ -mirror plane, $\sigma_s$ -glide plane, i - center of inversion (Krimm, Liang, and Sutherland, Ref. 11)

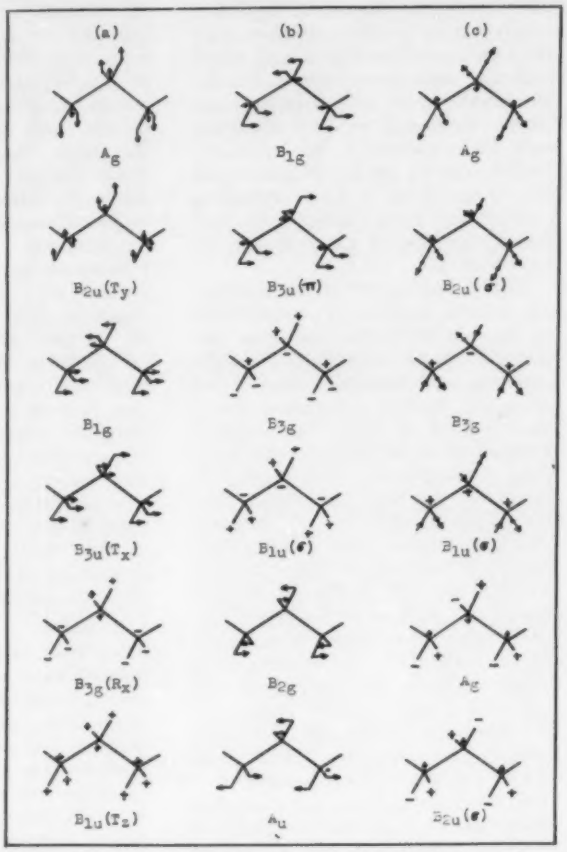


**Figure 3.** Symmetry modes of a single polyethylene chain (Krimm, Liang, and Sutherland, Ref. 11)

lene chain are shown in Fig. 3 Finally, the symmetry analysis predicts which normal modes will exhibit infrared activity and which will exhibit Raman activity. It will be noted that in this case the infrared active modes are Raman inactive, and vice versa, which is always a consequence of the presence of a center of symmetry in a molecule.

We see therefore that a symmetry analysis characterizes quite thoroughly the nature of the expected spectrum without requiring any detailed knowledge about the molecule other than its structure. In this connection four points must be made. First, the full structure must be used. In the case of polyethylene, the crystal contains two chains per unit cell, and the complete analysis (Ref. 11) included this result. Second, the above symmetry analysis deals only with the crystalline material, i.e., that part in which a translational periodicity exists. (This corresponds to the use of a factor group analysis, which physically means that only those modes will exhibit infrared or Raman activity in which motions of corresponding atoms in all unit cells are in phase.) Most polymers contain a more or less significant portion of disordered or amorphous chains. The lower symmetry of the chains in this portion of the material results in a relaxation of the selection rules, which in general implies the activity in either spectrum of more modes. Thus, we expect the amorphous chains to give rise to more bands than the crystalline. (In addition, other rotational isomers which can exist in the amorphous phase can give rise to new frequencies since basically they represent new structures.) Third, when there is more than one chain per unit cell in the crystal the possibility of interchain interactions exists, and these can give rise to splittings of some of the bands. This is clearly the case for polyethylene (Ref. 8). It is

**Table I. Character Table for Single Extended Polyethylene Chain**

| $D_{2h}$ | E | $C_2(z)$ | $C_2(y)$ | $C_2^s(x)$ | i | $\sigma(xy)$ | $\sigma_s(xz)$ | $\sigma(yz)$ | $n_i$ | T | T' | R' | $n'_i$ | IR | R |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_g$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 0 | 1 | 0 | 2 | f | p |
| $B_{1g}$ | 1 | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 2 | 0 | 1 | 1 | 0 | f | d |
| $B_{2g}$ | 1 | −1 | 1 | −1 | 1 | −1 | 1 | −1 | 1 | 0 | 0 | 1 | 0 | f | d |
| $B_{3g}$ | 1 | −1 | −1 | 1 | 1 | −1 | −1 | 1 | 3 | 0 | $R_x$ | 1 | 1 | f | d |
| $A_u$ | 1 | 1 | 1 | 1 | −1 | −1 | −1 | −1 | 1 | 0 | 0 | 1 | 0 | f | f |
| $B_{1u}$ | 1 | 1 | −1 | −1 | −1 | −1 | 1 | 1 | 3 | $T_z$ | 0 | 1 | 1 | a | f |
| $B_{2u}$ | 1 | −1 | 1 | −1 | −1 | 1 | −1 | 1 | 3 | $T_y$ | 0 | 0 | 2 | a | f |
| $B_{3u}$ | 1 | −1 | −1 | 1 | −1 | 1 | 1 | −1 | 2 | $T_x$ | 0 | 1 | 0 | a | f |

**f: forbidden, a: active, p: polarized, d: depolarized**

therefore quite important to know which bands in the spectrum arise from the crystalline regions and which from the amorphous regions. Finally, we might remark that in many cases where the overall polymer chain has very little symmetry, the symmetry analysis can be applied to portions of the chain. Such a local symmetry analysis has been applied with success to the phenyl group in polystyrene (Ref. 17).

The second aspect of the theoretical analysis involves the computation of the normal modes and their frequencies from knowledge of the structure and internal forces of the molecule. Such a calculation would then permit a fairly unambiguous assignment of the bands in the spectrum. Unfortunately, very few calculations of this type have been done for polymers. Only for the simplest, viz., polyethylene, have detailed computations been made (see references 14-30 in Ref. 26). In the case of polytetrafluoroethylene it has been possible (Ref. 15) to fruitfully make use of the results for polyethylene. In other instances (Ref. 18), crude calculations of this type for portions of a chain have been useful in helping to assign frequencies. There is no doubt but that more calculations of this kind are needed, nor that they represent an important approach to the basic understanding of the spectra of high polymers.

*Experimental.* The experimental aspect of the analysis is not only one of obtaining infrared (and Raman) data, but encompasses the problem of securing a range of information which will serve to yield a complete assignment of the spectrum, i.e., to identify all of the observed bands with the predicted normal modes. To achieve this goal requires a very broad experimental attack. The techniques for such a program, some recently developed and applied, others older, are considered below.

1. *Far Infrared Spectra.* In order to be able to make a complete spectral assignment it follows that we must have complete data. Yet until recently it was most common to obtain infrared absorption spectra of polymers only in the NaCl prism region, which covers the range of about 650-5000 $cm^{-1}$. The higher frequency regions are easily investigated (e.g., with quartz optics), but are not of primary interest because only overtone and combination bands occur there. The region of frequencies lower than 650 $cm^{-1}$, though more difficult to investigate, is however of immediate interest since fundamental frequencies are to be found there. Unfortunately, little work has been done in this region. Commercial spectrometers are presently being fitted with prisms (such as CsBr) which cover the range from 650 $cm^{-1}$ down to about 250 $cm^{-1}$, but work still farther out in the infrared (i.e., at lower frequencies) requires the use of a grating spectrometer. Existing commercial instruments have been adapted to this purpose (Ref. 21), and there are indications (Ref. 22) that commercial far infrared spectrometers will soon be available. The study of this low frequency region provides an important part of the data needed for a complete assignment of the spectrum, and the first systematic study of polymer spectra in this region (Ref. 14) was undertaken with this view in mind. It is to be hoped that the fruits of this work will demonstrate the desirability in future studies of having such extended spectral coverage.

2. *Raman Spectra.* As we noted in connection with the spectrum of polyethylene, not all normal modes of a molecule are necessarily infrared active This means that the infrared data do not always provide experimental information on the entire vibrational spectrum. Since most of the infrared inactive modes are Raman active it is clearly desirable to also have the Raman spectrum of the polymer. In cases where this has been available (Refs. 17, 26) the analysis has been made easier and more complete. The difficulties in obtaining Raman spectra of polymers seem to be related primarily to the problem of preparing appropriate specimens. The usual troubles are that the specimen scatters a great deal of light (primarily a result of its spherulitic morphology) and that it gives rise to a strong fluorescent background (presumably due to impurities). The latter problem is the most troublesome, but there are indications (Ref. 27) that it can be overcome. From the viewpoint of a complete spectral analysis of a polymer the effort to secure Raman spectra is highly important.

3. *Deuteration Studies.* The object of an assignment is to identify the modes which give rise to specific spectral bands. In the absence of detailed normal frequency calculations, this can in part be achieved by use of the group frequency concept, which identifies certain regions of absorption with particular chemical groups. It frequently happens, however, that absorption in a given region is common to two or more groups, thus making the identification of a band ambiguous. Any technique, therefore, which can separate out a particular set of normal vibrations is of great importance. The substitution of deuterium for part or all of the hydrogen in a molecule accomplishes just this: it identifies the bands arising from modes involving primarily the motion of hydrogen atoms. This is achieved because, whereas the forces are unchanged by the substitution of D for H, the mass of the nucleus involved in the vibration is increased by a factor of 2. Modes involving the motion of this atom will therefore decrease in frequency upon substitution by approximately $\sqrt{2}$ (usually by a factor of from 1.3 to 1.4). Since other modes are, to a first approximation, unaffected by such substitution, the bands which shift to lower frequency on deuterium substitution are thus identified as hydrogen modes. If selected kinds of hydrogen atoms can be substituted, then it is possible to break down the identification even further, and in some cases—such as the alcohols—to demonstate (Ref. 12) the existence of interactions between modes which would have, without additional evidence, been considered as separable group modes. Deuteration studies provide an important tool for identifying with certainty particular bands in the spectrum, and thus beginning to unravel the assignments of others.

4. *Polarized Spectra.* Another means of identification is possible if oriented specimens are studied in polarized infrared radiation. It was mentioned earlier that a condition for infrared absorption is that there be a changing dipole moment, or transition moment, during the particular normal vibration of the molecule. This is not the entire story: it is also necessary that there be a component of the electric field of the incident radiation along the direction of the transition moment. If the two are perpendicular to each other no absorption can occur. By orienting a structure (say by stretching a polymer film) we rigidly specify the directions, with respect to external axes, of the transition moments associated with the normal modes. It then follows that maximum absorption will occur when the electric field of the incident polarized radiation is parallel to the moment direction. Thus, if our assumptions about the structure are correct, the dichroism of bands in the spectrum (with respect to a defined structural direction) permits us to say something of their origin. For example, the character table for poly-

ethylene (Table I) prescribes that $B_{2u}$ modes will be polarized parallel to the chain axis whereas $B_{1u}$ and $B_{3u}$ modes will exhibit polarization perpendicular to this axis. The polarization data do not unambiguously identify all of the separate modes within each species, but when taken in conjunction with the other experimental data the problem of assignments is brought much closer to a solution.

5. *Analogue Spectra.* Another aid in making assignments for high polymers is to study the spectra of low molecular weight analogue molecules, preferably as single crystals. There are at least two main reasons for this. First, small molecules are more susceptible to a detailed analysis, and may therefore provide a secure basis for understanding the spectra arising from portions of the high polymer molecule. Thus, for example, the extensive and detailed work on the spectra of benzene and substituted benzenes was a prime factor in achieving an assignment of the spectrum of polystyrene (Ref. 17). Second, such analogue molecules are usually obtainable as single crystals, which means that certain important aspects of the polarized spectrum can be studied which would have been difficult to do with the oriented polymer, whose crystal structure cannot be as uniquely oriented as can a single crystal. For example, the prediction of an interaction splitting in the spectrum of crystalline polyethylene (Ref. 11) could be checked by studying single crystals of n-paraffins (Ref. 8) in a manner which was not possible with the oriented polymer. This is because the theory predicts that the components of the interaction-split doublet should each be polarized along a different one of the two crystal axes perpendicular to the chain axis. Whereas it is not possible to uniquely orient a polyethylene film in order to investigate this point, it is feasible to study a paraffin single crystal with radiation propagating along the chain axis direction and polarized separately along the two perpendicular crystal axes. In this way the theoretical prediction concerning polyethylene could be checked. Again the situation has been that too few studies of this type have been carried out in conjunction with the investigation of high polymer spectra. Further progress in this direction is clearly called for.

6. *Specimen Variation.* Because the usual polymer spectrum represents a superposition of bands due to amorphous and crystalline components, it is necessary to have experimental ways of distinguishing between the contributions of these two. If a crystalline analogue molecule is available (such as n-parafins are to polyethylene), then its spectrum serves to identify the crystalline contribution to the polymer spectrum. If such materials are not available, it is nevertheless usually possible to produce variations in crystallinity in the polymer, and thus to identify, by their changes in intensity, the bands associated with the two phases. For example, if a polymer is melted (so that x-ray diffraction patterns reveal no crystals), the bands which disappear must be representative of the crystalline phase whereas the spectrum of the molten polymer is representative of the amorphous contribution. Analogous deductions can be made by polymerizing the polymer under conditions which lead to differing degrees of crystallinity and by studying the spectra of solutions of the polymer. By means of such approaches we obtain additional means of deciphering, as it were, the origin of bands in the spectrum.

These represent the basic experimental techniques which must be applied to the study of high polymer spectra if a complete understanding of the spectrum is desired. In the past this has usually not been the immediate goal, in part because of the difficulties involved. Recent developments have shown that this goal is achievable with the concerted attack represented by the methods discussed in this section. That this goal is well worth achieving will, it is hoped, be demonstrated by some of the examples of the following section.

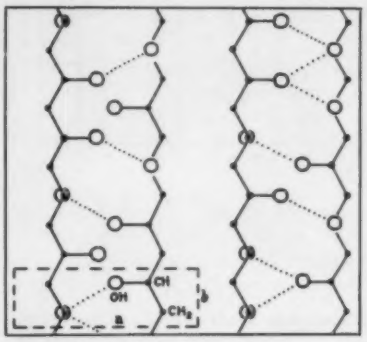


**Figure 4.** Mooney structure for polyvinyl alcohol (Ref. 24)

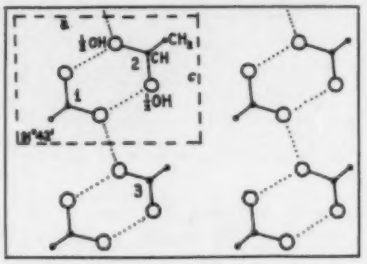


**Figure 5.** Bunn structure for polyvinyl alcohol (Ref. 2)

## Structural Results of Infrared Studies of Polymers

In this section we will be primarily concerned with some results of structural interest that have been a consequence of the detailed study of the infrared spectra of polymers. We will therefore not discuss in any detail the arguments for, nor the complete results of, the detailed assignment of any given spectrum. Rather we are interested here only in the structural implications of such assignments. It is worth noting that this structural information represents only a portion of the useful results of such an analysis.

The following examples are illustrative of a problem which is often encountered in the study of polymer structure. The most detailed method for determining molecular structure is, of course, x-ray diffraction. It has at least two limitations, however, with respect to the investigation of polymer structure. First, it is usually not possible to obtain as good x-ray diffraction data from polymers as can be secured from single crystals of smaller molecules, and therefore the results of the x-ray diffraction study are frequently not without ambiguity. Second, the location of hydrogen atoms in the structure, which is in general a difficult x-ray diffraction problem, is essentially impossible for polymer structures because of the paucity of data. Spectroscopic structural studies are therefore of great importance since they can provide additional evidence for the correctness of a structure (often by deciding between alternative models), and because they do furnish a fairly unambiguous method for locating hydrogen atoms. These two themes underlie the cases we will now consider.

*Polyvinyl Alcohol.* Two structures have been proposed for polyvinyl alcohol, one by Mooney (Ref. 24) and one by Bunn (Ref. 2), on the basis of x-ray diffraction studies. These are shown in Figs. 4 and 5 respectively. The x-ray evidence seems to favor the Bunn structure, but the case is not firmly conclusive. In this instance, on the basis of the polarization properties of certain of the bands in the infrared spectrum, it is possible to eliminate one structure and provide

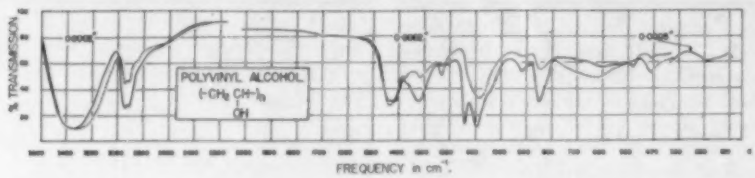


**Figure 6.** Infrared spectrum of oriented polyvinyl alcohol. Curves indicate transmission with electric vector perpendicular (—) and parallel (- - -) to the stretching direction (Krimm, Liang, and Sutherland, Ref. 13)

strong supporting evidence for the other.

In the Mooney structure the plane of the COH group is parallel to the chain axis. Therefore, in an oriented specimen we expect the normal mode corresponding to the motion of the hydrogen atom perpendicular to the plane—the out-of-plane hydrogen bending mode—to exhibit perpendicular dichroism with respect to the chain axis. In the Bunn structure, when the hydrogen atom is in a position to form the best hydrogen bond, the COH plane makes an angle of about 55° with the chain axis. The transition moment for the above deformation mode thus makes an angle of about 35° with the chain axis, and is therefore expected (Ref. 16) to exhibit parallel dichroism. If this mode can be identified and its polarization properties determined, it should be possible to make a decision between these two proposed structures. The infrared spectrum of polyvinyl alcohol has been analyzed in detail (Ref. 13) with the help of many of the techniques described in the previous section. A polarized spectrum of an oriented specimen is shown in Fig. 6. Deuteration studies on the polymer (as well as similar studies on alcohols) indicate that the OH out-of-plane deformation mode is to be assigned to the broad band at about 625 $cm^{-1}$. A glance at the spectrum in Fig. 6 now shows that this band has parallel dichroism, i.e., absorbs most strongly when the electric vector is parallel to the chain axis. The Mooney structure therefore cannot be correct, and the evidence at this point is in favor of the Bunn structure.

It must be noted that, whereas a structure is disqualified if it does not predict the observed dichroism, agreement between observed and predicted dichroism for one band does not prove a structure correct. This is because the dichroism measures only a property of the overall distribution of transition moments, and it is possible that different structures could give the same distribution. The case can be made stronger by examining the dichroism of several bands and attempting to check the agreement quantitatively. For example, it would be desirable to have the structure account for the practically negligible dichroism of the OH stretching mode at about 3340 $cm^{-1}$ as well as the moderately large parallel dichroism of the 625 $cm^{-1}$ band. This analysis has been undertaken for polyvinyl alcohol (Ref. 20), and the results are consistent with Bunn's structure. The infrared analysis thus disproves the Mooney structure and suggests that the Bunn structure, or one very much like it, must be the correct one.

*Polyvinyl Chloride.* The chain structure in the crystalline regions of polyvinyl chloride has to some extent been uncertain because of the poor quality of the x-ray diffraction patterns given by this material. Early x-ray studies (Ref. 5) showed that the oriented polymer had a fiber-axis repeat distance of about 5.1 A., and on this basis it was assumed that the chlorine atoms must alternate on either side of the plane of the carbon zig-zag chain. This is what we would now call a syndiotactic structure, and is illustrated in Fig. 7. More recent X-ray studies (Ref. 25) on better specimens seem to confirm this structure, but additional confirmatory evidence would be welcome.

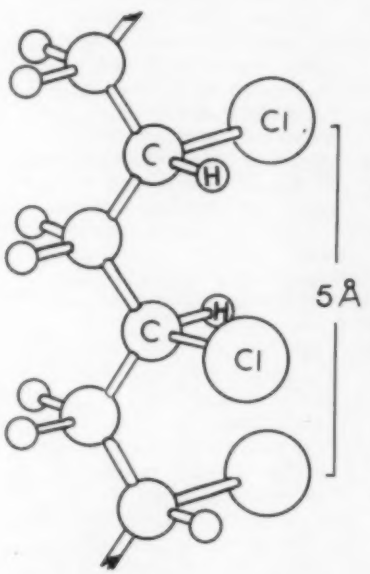


**Figure 7.** Structure of syndiotactic polyvinyl chloride.

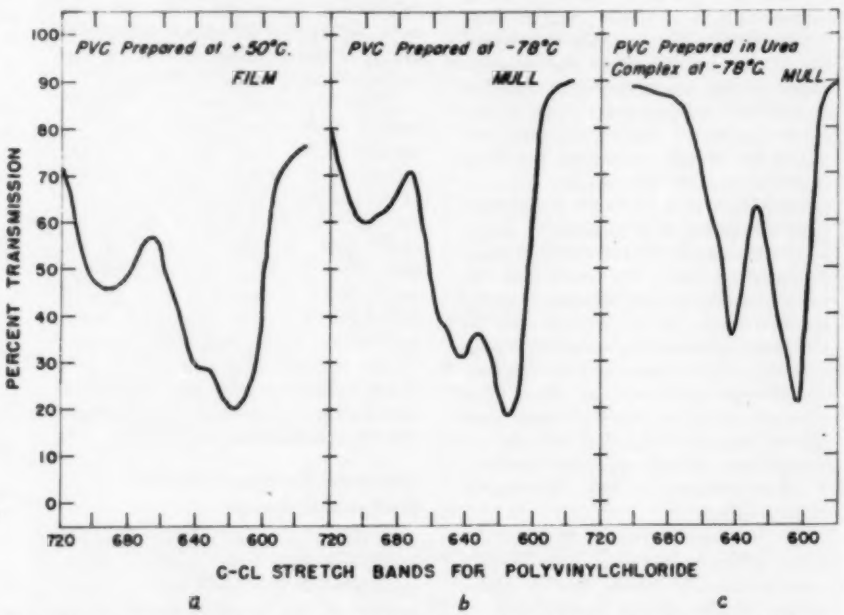


**Figure 8.** Spectra of various polyvinyl chlorides in the C-Cl stretching region (Krimm, Berens, Folt, and Shipman, Ref. 9)

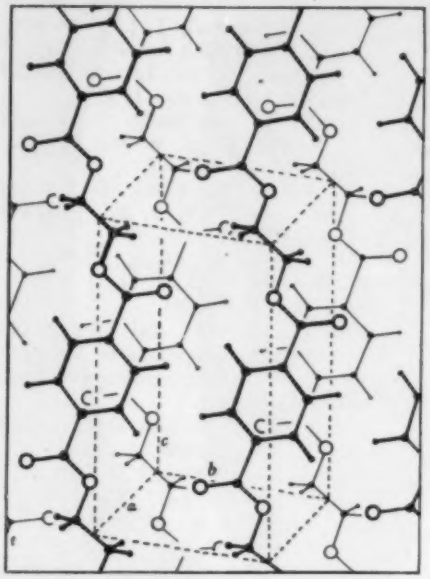

**Figure 9.** Daubeny, Bunn, and Brown structure of polyethylene terephthalate (Ref. 4)

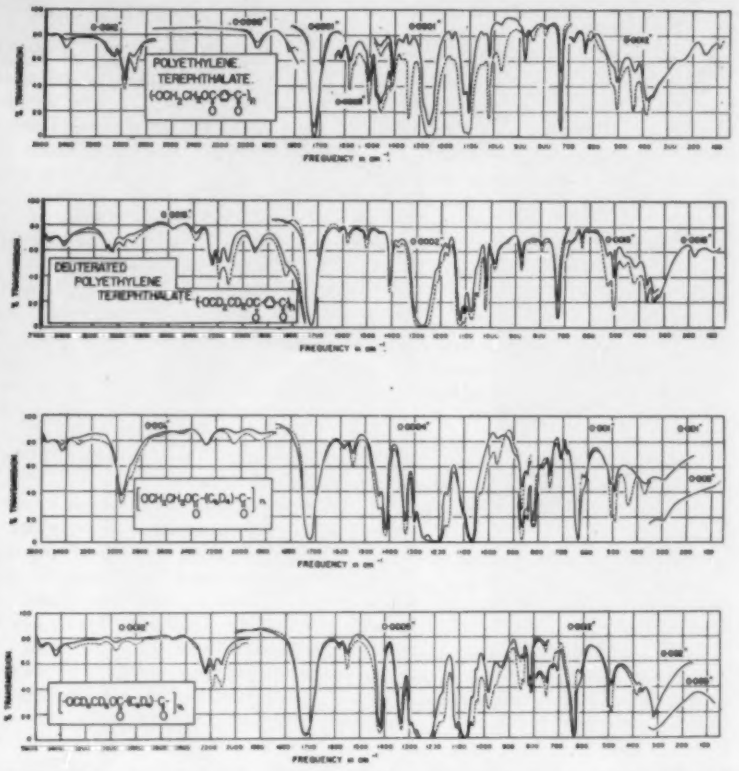


**Figure 10.** Infrared spectra of polyethylene terephthalate and deuterated analogues. Curves indicate transmission with electric vector perpendicular (—) and parallel (- - -) to stretching direction (Liang and Krimm, Ref. 19)

An analysis of the spectrum to be expected from syndiotactic polyvinyl chloride (Ref. 10) indicates that the C-Cl stretching modes in a planar zig-zag chain should give rise to two bands. Physically, this is due to the presence of two C-Cl groups in the repeat unit along the chain axis. If there is any interaction between the two groups, the vibrations are no longer independent but become coupled, giving rise to two normal modes in which the Cl atoms move respectively in phase and out of phase with each other. These modes will have slightly different frequencies, and we may therefore expect to see a doublet in this region of the spectrum, the separation of course being a function of the magnitude of the interaction. The spectrum of this region for a typical sample is shown in Fig. 8a, and it can be seen that there are at least three bands present, at 615 $cm^{-1}$, 635 $cm^{-1}$, and 693 $cm^{-1}$.

The seeming complexity of this absorption can be unraveled when we recall that rotational isomers of the polymer chain are present in the amorphous regions (Ref. 10), and that these give rise to different fundamental frequencies (Ref. 23). The rotational isomerism of small molecules containing chlorine has been studied in detail, and it appears that in secondary chlorides when the chlorine atom is trans to a hydrogen atom across the common C-C bond the characteristic C-Cl stretching frequency occurs in the region of about 600-640 $cm^{-1}$, whereas when the chlorine atom is trans to a carbon atom this frequency will be found at about 670-700 $cm^{-1}$. On this basis, and from additional experimental data, it has been suggested (Ref. 9) that the fundamental frequencies of a planar zig-zag syndiotactic chain are to be associated with bands at 605 $cm^{-1}$ and 642 $cm^{-1}$. These data consist of spectra of more highly crystalline polymers which have been prepared by polymerization at low temperatures or in a urea canal complex. Spectra for such polymers are shown in Fig. 8, b and c, where it can be seen that with increasing crystallinity (as determined by X-ray diffraction patterns) there is an enhancement in relative intensity of bands at 605 $cm^{-1}$ and 642 $cm^{-1}$ whereas the 615 $cm^{-1}$ and 693 $cm^{-1}$ bands become practically undetectable.

These results lead to the following structural conclusions. If the assignments of the 605 $cm^{-1}$ and 642 $cm^{-1}$ bands are valid (as they seem at present to be), then the spectral evidence supports the existence of a planar zig-zag syndiotactic structure for portions of the polyvinyl chloride chain, the amount of this structure being a function of the conditions of preparation of the polymer. The 615 $cm^{-1}$ band most probably arises from isomeric structures in which a chlorine atom is trans to a hydrogen atom but in which the interaction present in a planar zig-zag syndiotactic chain does not exist. These could be either syndiotactic chains which are not in the planar zig-zag form (such as in the amorphous regions) or portions of planar zig-zag chains which have an atactic arrangement of chlorine atoms (in which case the interaction between adjacent chlorine atoms is not expected to occur). The 693 $cm^{-1}$ band undoubtedly arises from structures in which a chlorine atom is trans

to a carbon atom. These could be either syndiotactic or atactic portions of chains in the other possible nonplanar zig-zag configuration, or an isotactic helical structure of the $(AB)_n$ type (Ref. 3) which also places chlorine trans to carbon. Although some of these latter alternatives remain to be clarified, it is evident that the detailed spectral study of polyvinyl chloride has greatly furthered our understanding of the structure of this polymer.

*Polyethylene Terephthalate.* The basic structure of polyethylene terephthalate has been determined by a very detailed X-ray diffraction study (Ref. 4), made possible by the good diffraction patterns obtainable from an oriented specimen. This structure is shown in Fig. 9, and was used as the basis of a complete spectral analysis (Ref. 19). As we shall see, it requires modification in some details.

In the present case it was possible to bring to bear a wide range of data and techniques in the analysis of the spectrum. In Fig. 10 are shown infrared spectra of polyethylene terephthalate and several of its deuterated analogues. It will be noted that the spectra extend to the far infrared region, and also that polarized spectra were obtained. In this instance there were also available information on the changes in band intensities on crystallization, spectra (both infrared and Raman) of low molecular weight analogue compounds, and assignments of para disubstituted benzenes. The sum of these data has made possible what appears to be a reasonable and self-consistent assignment of the entire spectrum. Two results of structural significance stand out from this assignment.

First, it appears that the orientation of the two $CH_2$ groups in the above structure is not correct. If the orientation of these groups were as given by the structure, then it can be shown (Ref. 19) that the $CH_2$ stretching, bending, and rocking modes should exhibit perpendicular dichroism in an oriented specimen. Yet analysis of the spectrum shows that the bands assignable to these vibrations all have parallel dichroism (cf. the $CH_2$ stretching modes at 2908 $cm^{-1}$ and 2970 $cm^{-1}$). The implication is that the orientation of these $CH_2$ groups in the proposed structure is not correct. It is interesting to note that the authors (Ref. 4) themselves observe that the location of these carbon atoms is the least reliable part of the structure determination. It has been found (Ref. 19) that a chain structure can be built in which the $CH_2$ groups are oriented so as to give the correct dichroism. This chain will fit in the same unit cell, but must be oriented somewhat differently. The agreement between this slightly revised structure and the X-ray data has not been determined as yet, so it cannot be said for certain that it is correct. The spectral data do, however, indicate the need for a revision of the Daubeny, Bunn, and Brown structure.

The second point has to do with the mechanism of disorientation of the chains. On the basis of a preliminary spectral analysis, it had appeared (Refs. 29, 6) that the polymer chain departs from its extended crystalline form primarily by rotational isomerism about the $CH_2$-$CH_2$ bond. The recent analysis (Ref. 19) shows that the spectral bases for the above conclusion are not tenable, and suggests that other rotations may be of importance in this respect. For example, it appears that in the amorphous phase there are significant departures from the planarity of the - CO - $C_6H_4$ - CO- portion of the molecule which exists in the crystalline phase. The spectrum thus provides some indication of the structure of the chains in the amorphous regions.

## Conclusion

This brief discussion has attempted to indicate the potentialities of a complete spectroscopic analysis of high polymers with respect to information that can be obtained about molecular structure. As was pointed out, this is not the only kind of result obtained: spectroscopic studies also provide information about intra- and intermolecular forces. The primary theme of this article is that detailed information of both types is obtainable if the analysis aims at a complete understanding of the spectrum of the polymer rather than just a cursory study of some of the bands. It has been shown in several examples how a study of this kind has clarified our understanding of the polymer structures involved.

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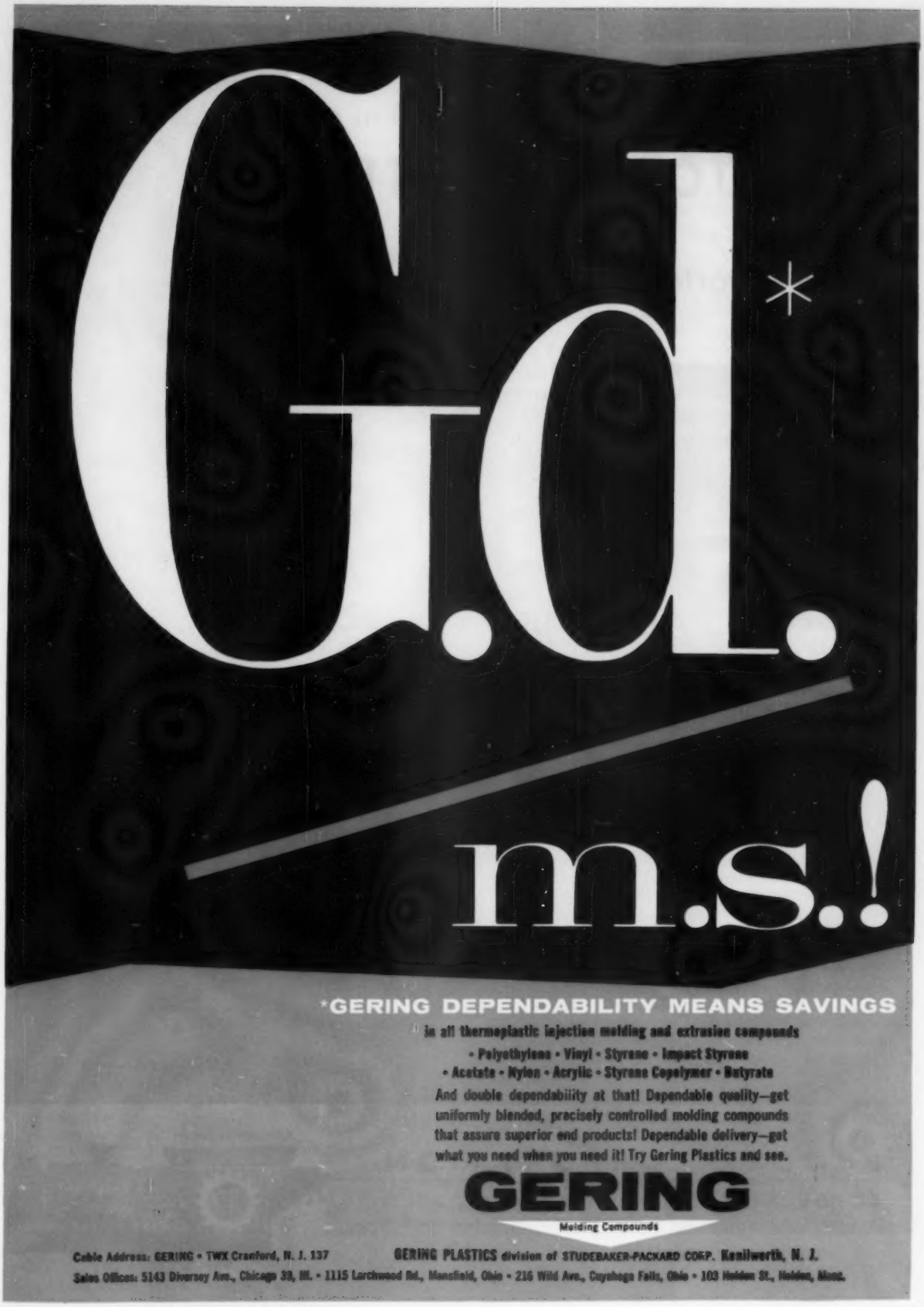
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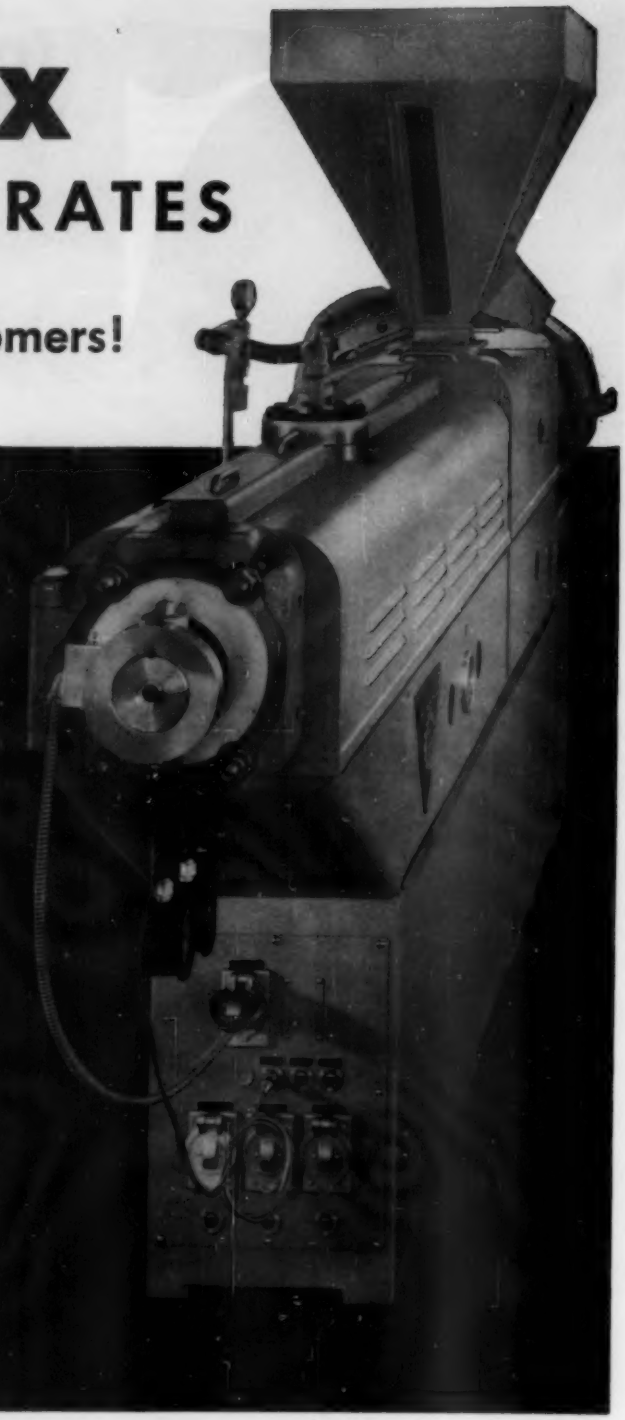

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| ABS Sheet, vented | 200 |
| Rigid vinyl pipe from dryblend | 170 |
| Polyethylene on cellophane | 170 |
| 3½" (40 H.P.) | |
| Vinyl garden hose | 480 |
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# The Application of Flexible Conduits in Extrusion

**A new development in extrusion: Use of a tube of Teflon and flexible steel hoses for connecting extruders to various dies and forming devices.**

Speaking of Extrusion

**Edited by: B. H. Maddock**
*Union Carbide Plastics Co.*

Plastic melts can be conveyed from an extruder through a flexible conduit. Several uses for this rather simple process come to mind immediately: (1) extrusion welding; (2) casting of massive shapes; (3) connecting two extruders to the same die, for instance for multicolor extrusions; (4) placing colored decorative patterns on plastic or non-plastic substrates; (5) multiple coatings of different resins applied to a substrate in one operation by using two dies, one positioned by means of a flexible conduit. More applications will undoubtedly develop.

Some of the uses which have already been demonstrated include extrusion welding, extrusion casting of massive shapes, and preparing decorative panels with colored beading. Polyethylene, nylon, and acrylic resins have been processed through conduits of this type.

## Construction

Conduits which have been found suitable for conveying plastic extrudates consist of three components, all commercially available.

(1) The hose itself can be either an overbraided all-steel corrugated hose or a tube of a Teflon® TFE-fluorocarbon resin reinforced externally with stainless steel braid.

(2) The hose is first wrapped with a glass tape to provide electrical insulation. A tape heater is then wrapped around the hose to maintain the extrudate at the desired temperature during its passage through the conduit. A thermocouple is embedded between the heater and the hose.

(3) A sleeve of asbestos insulation is applied over the completed assembly to reduce heat loss and to facilitate handling.

A picture of the flexible conduit assembly used for extrusion-welding is shown in the photograph.

## Operation

The conduit may be connected to the extruder by means of a simple adapter. This adapter should be tapped for three instruments: a stock thermocouple, a Bourdon pressure gauge and a rupture disk assembly. These devices aid in protecting the hose against excessive pressure and temperature.

Before the start of the extrusion operation, the conduit should be preheated to allow it to reach the temperature of the melt to be processed through it. If the conduit is filled with cold resin (after a prolonged shut down), preheating for at least one hour may be required. This applies particularly to hose lined with TFE resin because this material is a poor conductor of heat.

## The All-Steel Conduit

All-steel conduits are able to resist the highest temperatures and pressures. In our experimental work we employed 5' long, ¾" ID overbraided corrugated stainless steel hose (such as 'Rex-Weld' RW 81, Flexonics Corporation, Maywood, Illinois). We subjected it to pressures as high as 3000 psi and temperatures up to 600°F.

Two characteristics which may be disadvantageous should be borne in mind when assembling an all-steel conduit:

(1) The corrugated construction of the steel hose may enable resin to lodge in the pockets and decompose on long exposure to heat. However, no difficulty of this nature has been encountered with Alathon® polyethylene resins at high extrusion rates.

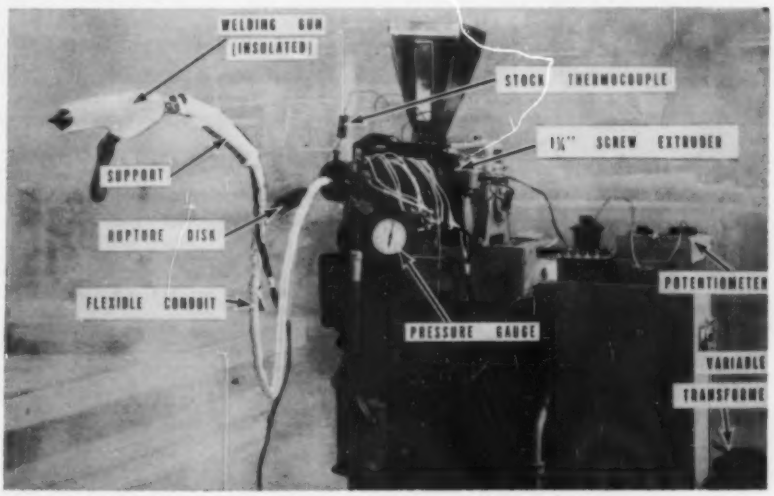
(2) The all-steel hoses are less flexible than hoses lined with TFE resin. However, they are more resistant to overflexing and kinking.

## The Overbraided Tubing of TFE Resin

Overbraided tubing of a Teflon® TFE-fluorocarbon resin offers the advantage of a flexible conduit with smooth inside walls, which reduces the chance of material hold-up.

On the other hand, the application of conduits containing a tube of TFE resin are limited to lower temperatures and lower pressures than the all-steel construction. In our experimental work, we tried not to exceed 1000 psi pressure and 550°F. temperature when using tubing lined with a TFE resin.

Sources of such hoses include: Aeroquip Corporation, Jackson, Michigan; American Brass Company, Waterbury, Connecticut; B. F. Goodrich, Akron, Ohio; Raybestos-Man-




Welding gun connected to extruder with flexible conduit.

**Table I. Conditions for Extrusion of Polyethylene Through a Flexible Conduit**

**Resin:** Alathon® 37; Melt Index 12
**Stock Temperature (at adapter):** 520°F.
**Conduit Temperature:** 500°F.
**Pressure (at adapter):** 600 psi
**Output:** 125 lbs./hour
**Flexible Conduit:**
*Hose*: "Fluoroflex" T; R 3800-12-"L", Resistoflex Corporation, Roseland, New Jersey; ⅝" x 5'
*Heater*: ⅛" x ½" x8' "Briskeat"; 384 watts, heavy duty, The Briscoe Company, Columbus, Ohio

**Table II. Conditions for Extrusion-Welding**

**Material to be welded:** ½" stock of Alathon® 10
**Welding Resin:** Alathon® 16
**Stock Temperature (at adapter):** 535°F.
**Temperature of Flexible Conduit:** 535°F.
**Temperature of welding gun:** 580°F.
**Welding gun tip:** 30° cone
**Pressure (at adapter):** 800 psi
**Extrusion Rate:** 4-6 lbs./hour
**Rate of Welding:** 2'/minute
**Flexible Conduit:**
*Hose*: "Fluoroflex" T; R 3800-8-"L", Resistoflex Corp., Roseland, New Jersey; 13/32" x 6'
*Heater*: ⅛" x ½" x 8' "Briskeat"; 384 watts, heavy duty, The Briscoe Company, Columbus, Ohio

hattan, Inc., Mannheim, Pennsylvania; Resistoflex Corporation, Roseland, New Jersey; Titeflex, Springfield, Massachusetts.

The liner within the conduit should be protected against damage during shut-downs. Before the polymer melt solidifies, most of it should be forced from the hose. This may be done by disconnecting the hose from the extruder, and injecting a high-vacuum silicone grease through a special adapter.

This precaution serves several purposes:

(1) Couplings and adapters, not easily heated by the tape heater, are not left filled with plugs of solid polymer which must be completely fused before resuming the extrusion.

(2) Less warm-up time is required for the whole conduit to be operable again; consequently there is less chance for local overheating due to too rapid warm up.

(3) Any danger that the polymer remaining in the conduit may damage the liner of TFE resin while the resin cools and shrinks linearly is considerably reduced.

## Pressure Drop Within The Conduit

The viscosity of the resin, the diameter of the conduit, and the length of the conduit will all influence the amount of pressure required to extrude the melt at the desired rate. This pressure must not exceed the maximum recommended by the manufacturer of the conduit. Hence, it is helpful to be able to predict the resistance to flow through the conduit.

The pressure drop for a given resin, a given conduit geometry and a given set of operating conditions can be calculated using the Newtonian flow equation for a round orifice. (A sample calculation is given in Table III). In order to use this equation, the viscosity of the resin at the low shear rates encountered in the flexible conduit must be known. Viscosity data over a wide range of shear rates may be found in the book "Processing of Thermoplastic Materials", E. C. Bernhardt (ed.). Reinhold Publishing Company, 1959.

## Application in Extrusion-Welding

The flexible conduit has been used successfully to convey molten extrudate to a welding gun. The actual welding operation consists of positioning the welding gun between the members to be joined and moving it at such a rate that the channel between them is filled evenly with plastic melt. The heat contained in the melt must soften the surfaces to be joined and fuse them to the melt. For this reason the temperature of the melt should be as high as possble.

The welding gun used in this work consists of a heated cylinder with a handle and an exchangeable tip. Three ¼" diameter channels 8" long convey the melt through the cylinder. This design affords maximum opportunity for heat transfer, allowing the 240 watt band heater to raise the temperature of the melt from 550°F (limit of safe operation of the hose) to as much as 650°F at normal welding rates.

Using this technique, rates of over two feet per minute were achieved in extrusion-welding sections of Alathon® 10, up to one-half inch thick.

Extrusion-welding as such is not new but has heretofore been confined to use of the molten polymer directly from a nozzle rigidly attached to the extruder, which necessitated awkward maneuvering of the pieces being welded. Flexible conduit eliminate this fault.

## Conclusion

The above illustration of the use of the flexible conduit in extrusion-welding is offered only as one typical example. Flexible conduits provide a new means for conducting polymer melts between various plasticating and forming devices, and thus are expected to give the processor a valuable new tool for many applications.

**Table III. Sample Calculation of Pressure Drop in a Flexible Conduit**

**Problem:** Calculate the pressure drop per foot of ⅝" hose to be used to extrude Alathon® 17 (Melt Index 20) at a rate of 100 pounds per hour at 525°F.

**Equation:**

$$Q = \frac{\pi R_o^4 P}{8 \mu Lo} \quad *$$

$R_o$ = radius = ½ x ⅝" = 0.31"
Lo = length = 12" (to calculate pressure drop per foot)
P = pressure drop, psi
Q = volumetric flow rate, in.³/sec.
$\mu$ = melt viscosity, lb-sec./in.²

**To Calculate Q:**

Density of polyethylene at 525°F. = 0.72 gms/cc
Output = 100 lbs./hr. x 454 gms/lb. x 1/3600 hrs./sec.
Output = 12.6 gms/sec.
Q = 12.6 gms/sec. x 1/0.72 cc/gm x 0.061 in.³/cc
Q = 1.06 in.³/sec.

**To determine $\mu$, the shear rate must be calculated:**

$$\text{Shear rate} = \frac{4Q}{\pi R_o^3} \quad * = \frac{4 \times 1.06}{3.14 \times (0.31)^3} = 45 \text{ sec.}^{-1}$$

$\mu$ (at a shear rate of 45 sec.$^{-1}$) = 0.01 lb.-sec./in.²*

**From the original equation:**

$$P = \frac{Q8 \mu Lo}{\pi R_o^4}$$

$$P = \frac{1.07 \times 8 \times 0.01 \times 12}{3.14 \times 0.31^4} = 36 \text{ p.s.i./ft.}$$

* From "Processing of Thermoplastic Materials," E. C. Bernhardt (ed.) Reinhold Publishing Company, 1959.

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# Molding Cycles

**FOR AUTHORITATIVE ANSWERS send your questions on molding to Louis Paggi, Sales Service Laboratory, Polychemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Delaware.**

**Edited by: Louis R. Paggi, Consultant**
*E. I. du Pont de Nemours & Co., Inc.*

*More effective cooling of molds*

## How do you eliminate warpage in center–gated articles?

**Q–Can you offer suggestions for eliminating warpage occurring in center gated articles such as containers, lids, trays, etc. when such warpage is apparently not due to non-uniform wall sections or unbalanced mold temperature?**

A–Several conditions can contribute to warpage. Among them are:

1. Gates too large in cross-section.
2. Cavity not filled to a uniform density (locally over-packed or under-packed especially at or near the gate area). This condition can best be controlled with weigh feeding.
3. Rate of mold filling too slow.
4. Mold temperature too low or too high. Low mold temperature results in flow orientation and local stress formation. High mold temperature may result in local deformation.
5. Material temperature too low resulting in incomplete melting of the material.
6. Non-uniform temperature of the plastifying cylinder resulting in non-uniform melt temperature.
7. Cycle too short.

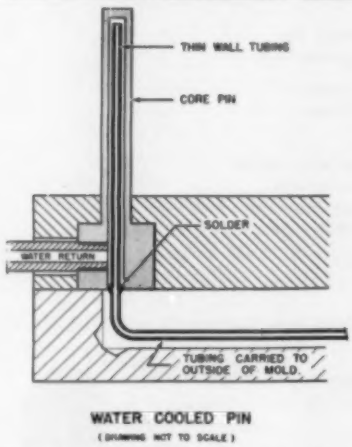


Figure 1. **Water cooled** pin. Note tube inserted into core pin as far as circulation of water permits. Note also tubing carried to outside of mold.

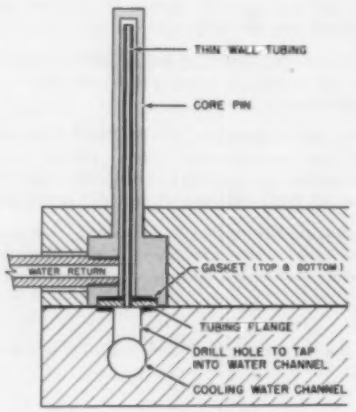


Figure 2. **Water cooled** pin showing thin wall tube which does not run beyond the base of the core pin.

We thank one of our readers for calling our attention to the need for clarifying the following paragraph appearing in the "Molding Cycles" column of the July issue of the S.P.E. Journal.

> "The most important feature of this design is the length of the thin wall tube. It should be held to an absolute minimum. The restriction to the flow of water resulting from the small diameter tube is therefore minimized."

This statement was misunderstood to mean restricting the length of that portion of the tube which is housed within the core pin. Actually, as seen in the sketch the tube should be inserted as far into the core pin as will permit circulation of water.

The reference to the important feature of this design as applies to the length of the thin wall tube is clarified in the two drawings. Note that in one case the thin wall tube is carried to the outside of the mold where it is attached to a water supply. (Fig. 1)

While this design is often employed for large diameter core pins because it is less costly to incorporate, it is not a satisfactory design for small diameter core pins because of the restriction of the flow of water resulting from the excessively long-small-diameter tube.

The other drawing shows the improved design featuring a minimum length of thin wall tubing, i.e., the small diameter tubing does not run beyond the base of core pin. (Fig. 2).

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# Moldmaking

**Edited by: Ernest J. Csaszar**
*Sales Manager, Newark Die Company, Inc., Newark, N. J.*

## Definition of a Moldmaker

**Ernest J. Csaszar**

In our last feature article we asked that you, our readers, submit either questions or specific items of design regarding the field of moldmaking. In this way this feature would be useful to those who want to share their knowledge as well as to those who are seeking answers to problems they have.

Of course, at the moment of the writing of this article, you are just about getting to read the last one. Therefore, not enough time has elapsed to get your questions or design information in. Please let this be a reminder for you to do so. Perhaps the balance of this article will serve to provoke your thinking into action.

### What is a Moldmaker?

If we are going to discuss problems, questions and answers, or items of design regarding the field of moldmaking it might be well for us to first take a look at just what sphere of influence we are to cover. What is a moldmaker? In the simplest of terms, we can say "a moldmaker is one who is engaged in the manufacture of molds". Of course, we cannot end it there. Let's look into the picture a bit further.

The design and construction of a mold for the plastics industry involves, at least, four other major considerations separate from the actual mold construction. They are: the part to be molded, the molder, the material to be used and the press in which the mold is to be run. In effect, the creation of a mold, and its ultimate operation, ties together the elements of part, material and press through the activities of the molder involved. Let's look at these elements one by one.

### Four Considerations

First, the part to be molded exercises the greatest single influence on the mold construction. It, in essence, is the foundation upon which all other considerations of design and construction are built. In short, the mold must ultimately produce the part desired. Often, it is necessary to go to great lengths to devise ingenious mechanisms, cam actions and the like, to accommodate the molding of intricate elements of part design.

Second, the molder must be satisfied in his requirements. The mold must contain features of design and construction upon which the molder can exercise his molding techniques. These considerations can vary from plant to plant, even for the same part. Here we consider such items as point of gating K/O pins, parting lines, finishing, warpage, distortion and others.

Third, the mold construction must accommodate the material to be used. We must consider the proper shrinkage allowances, bulk factors, mold temperature control, runner systems, type of gating, stripping of undercuts, draft allowances and the like.

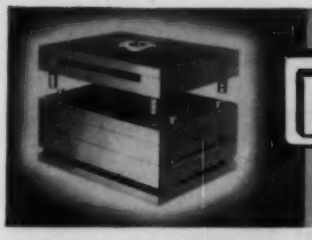
Fourth, the mold must fit the press to be used. The press K/O mechanisms, platten areas, nozzle details, clamping features, daylight, stroke, clamping pressure and auxiliary actions all become a factor of mold design and construction.

Now, perhaps we can write a more comprehensive definition of a moldmaker. Shall we say, "a moldmaker is one who is engaged in the design and manufacture of molds for the plastics industry with specific knowledge in the proper application of product design, molding techniques, material technology, and molding press design and operation, so far as these elements are related to mold construction."

### A Wider View

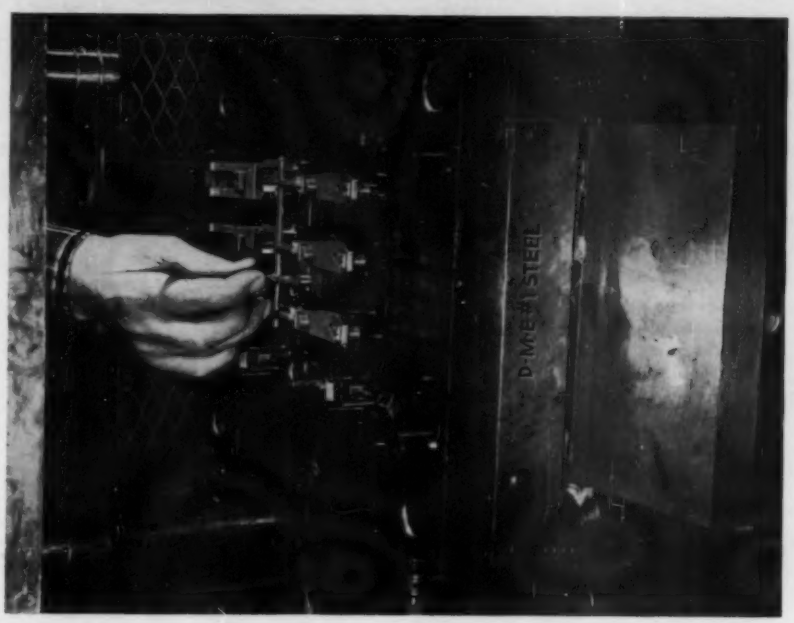
The point we would like to make is this: The art of moldmaking is not limited to the mere cutting of steel, hobbing, duplicating, fitting engraving, assembly and other elements of mold construction normally associated with this function. It is just as important for the moldmakers, as it is for any other industry segment, to be on the mailing lists of material manufacturers and press manufacturers regarding their technical data. Similarly, in this feature we should like to include this somewhat wider view of moldmaking.

With this in mind, let's get your contribution in. Perhaps we can hear from some of the press or materials people as to what you would like to see in mold construction to better accommodate special properties or features of operation.



# DME Mold Standards

DEDICATED TO QUALITY, SERVICE AND ECONOMY IN MOLDING

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59-A

National Action

# SPE Opens Its Doors to Students

BY JAMES R. LAMPMAN, CHAIRMAN, NATIONAL MEMBERSHIP COMMITTEE
AND JOHN M. BERUTICH, CHAIRMAN, STUDENT MEMBER SUBCOMMITTEE

**Edited by: Thomas A. Bissell**
*SPE Executive Secretary*

The Society of Plastics Engineers, by virtue of its newly revised Constitution, has provided a means for properly qualified students to join the Society. A regularly enrolled student pursuing a technical course at a recognized college or university who is less than 26 years of age, may take advantage of this new classification of membership in SPE. Student members may participate in all affairs of the Society other than voting or holding elective office. The student pays no initiation fee and only $5.00 per year in dues. Among the many advantages he will receive as a member of SPE is a subscription to the SPE Journal, which will furnish a great deal of practical assistance in each of its features and departments for the individual newly introduced to the plastics industry.

Each of us who takes an active part in the plastics industry will recognize this situation as an unusually fine opportunity to interest young technically trained men in our type of work. Students who have shown an interest in the plastics field should be encouraged by members to affiliate with our Society. Sections should organize committees to search out interested students in nearby colleges and invite them to their Section meetings. Some Sections are already working on effective student activity programs. Other groups have plans for sponsoring individual student memberships in their areas or for inviting several students to each meeting as guests of the Section. Certainly the funds of the Section can be used for no finer purpose than to assist and encourage young men interested in plastics engineering.

As soon as it was known that Student Memberships were available, inquiries were received as to the possibility of forming student SPE groups at schools where sizable numbers of students would be interested. One of the first groups to inquire were students of the plastics engineering course at Lowell Technological Institute, Lowell, Mass., who were interested in being chartered as "the first Student Chapter of the Society of Plastics Engineers, Inc." This group of approximately fifty men worked closely with members of the Eastern New England Section and, before the beginning of the summer season, had signed up enough Student Members to assure their claim to the first Charter assigned to a Student Branch of SPE.

The SPE National Council on June 12 approved the procedure (subject to rewording and possible modification by the Constitution and By-Laws Committee) for establishment of Student Branches of SPE. A group of students interested in forming a Student Branch of the Society may petition the National Council, SPE, for a charter provided that the following requirements are met:

1. The petition must be signed by ten or more Student Members of SPE, in good standing.
2. Evidence is provided that the group will be organized and will operate under the direct supervision of a faculty advisor who is an SPE member in good standing.
3. Evidence is provided that one of the geographic Sections of the Society has agreed to sponsor the proposed Student Branch.

Section sponsorship of individual members and of Student Branches is vitally important as an indication of interest and of willingness to offer general assistance. Perhaps equally important is the practical help that many Sections will be able to provide. Student Branches should have a very small financial burden but will need a great deal of help in planning programs and obtaining good speakers.

Some questions have arisen regarding use of the application blanks by prospective Student Members. The form is, of course, designed for applicants with industrial experience but can easily be adapted by the student. He need only substitute school address where business is requested, use *Student* as "Title or Position" and in "Record of qualifying experience" can enter "no industrial experience" or other applicable remarks. Other parts of the application form should apply to the student as well as anyone else and are self-explanatory. The sponsoring member can assist the Society by reviewing the application before it is forwarded to be sure it is complete. NOTE CAREFULLY that no money need accompany the application since there is no initiation fee involved. Dues will be billed after final election to membership. The use of the revised brochure "What SPE Can Do For *You*" will be very helpful in introducing our Society to all prospective members.

The Student Member gives all of us a triple opportunity—we can help interested young men find their place in industry; we can enlarge our own technical Society by enrolling vital young blood in the organization; and we can improve the plastics industry by convincing technical students that their future belongs in plastics engineering See this month's Membership Barometer on page 825.

## National Contest Spurs Fall Membership Drive

Announcement of an autumn national contest has been sent to all Sections by National Membership Committee Chairman, James R. Lampman. The prize: A large SPE banner on which the winning section's name and date are emblazoned. The contest started September 1, 1959 and will continue for four months, ending December 31st. The winner will be selected from SPE's 43 Sections by a simple formula—the ratio of new applications received during this period over total Section membership as of September 1st. Additional copies of the announcement are available from National Office.

# Technical Conferences

# NATEC

PROGRAM

## TUESDAY, 13 OCTOBER

9:00 AM to Noon—Joint Session on New Materials

### NEW THERMOPLASTIC MATERIALS

*Moderator: Louis Tallman, Dow Chemical Co.*

9:00 "POLYPROPYLENE—PROPERTIES AND PROCESSING"
Dr. R. A. Westlund and W. L. Dunkel, Enjay Co.

9:25 "ZERLON 150—A NEW MMA—STYRENE COPOLYMER"
Jack Little, Plastics Technical Service, Dow Chemical Co.

9:50 "BAKER PL-11—A NEW THERMOPLASTIC POLYMER"
Dr. C. H. Schram, J. T. Baker Chemical Co.

10:15 Intermission

### NEW THERMOSETTING MATERIALS

*Moderator: Milton Buck, L. H. Butcher Co.*

10:30 "EPOXY MOLDING COMPOUNDS—NEW FIELD FOR MOLDERS" Paul Fina, Fiberite Corp.

10:55 "ENCAPSULATION WITH ALKYD MOLDING COMPOUNDS"
John T. Long, Allied Chemical Corp.

11:20 "POLYURETHANE FOAMS"
Richard Hayes, American Latex Corp.

12:00 LUNCHEON—*Chairman*, Dr. Raymond Seymour, Alcylite, Speaker Introduction, *Henry Kveen, North American Aviation*
Speaker: William Zisch, Vice President and General Manager, Aerojet-General Corp.

2:00 Joint Session—Moderator, Carl Seybold, Consultant
"QUALITY CONTROL IN MANUFACTURING"
Dr. E. P. Coleman, UCLA.
Afternoon—Two Concurrent Sessions on Processing

### PROCESSING THERMOPLASTICS

*Moderator: Harold Kotkin, Plastic Process Co.*

2:45 "DETERMINATION OF AIR ENTRAINMENT OF VINYL PLASTISOLS"
Carl S. Seybold, Jr., Consultant

3:15 "INCREASING PLASTICATING CAPACITIES OF INJECTION MOLDING MACHINES"
Don Peters and J. N. Scott, Phillips Chemical Co.

3:45 "EQUIPMENT AND TECHNIQUES FOR THE EXTRUSION OF THERMOPLASTIC MATERIALS"
N. C. Taylor, Eastman Chemical Products

### PROCESSING THERMOSETTING MATERIALS

*Moderator: Leonard Costanza, Douglas Aircraft Co.*

2:45 "POLYMER STRUCTURE VERSUS MECHANICAL PROPERTIES OF SILICONE-REINFORCED PLASTICS"
Andrew M. Stein, Boeing Airplane Co.

3:15 "STRUCTURAL FILAMENT-WOUND PREPREGS"
L. J. Geiger, Amercoat Corp.

3:45 "AMINE BORANES AND ALKOXY BOROXINES AS POTENTIAL NEW CURING AGENTS FOR EPOXY RESINS"
Dr. Henry Lee and C. Klopfenstein, Epoxylite Corp.

## WEDNESDAY, 14 OCTOBER

9:00 Joint Session *Moderator: Paul Metzger, Hercules Powder Company*

"STATUS OI AMENDMENTS TO THE FOOD AND DRUG LAWS"
John Kuniholm, Hercules Powder Company
Two concurrent sessions on end uses

### THERMOPLASTIC MATERIALS

*Moderator: Al Ray, Ray Products*

9:45 "END USE MARKETS BY BLOW MOLDING PROCESS"
T. W. Mullen, Celanese Corp.

10:15 "LABORATORY AND FIELD EVALUATION OF PLASTIC PIPING SYSTEMS" Harold Kotkin, Plastics Process Co.

10:45 Intermission

11:00 "INJECTION BLOW MOLDING" Don Peters, Dan Perry, and J. N. Scott, Phillips Chemical Company

11:30 "FLUIDIZED BED COATINGS"
John Delmonte and Woody Crank, Furane Plastics

### THERMOSETTING MATERIALS

*Moderator: Rod Maybee, Shell Chemical*

9:45 "DESIGN, FABRICATION, AND ERECTION OF THE 110-FOOT DIAMETER SPACE-FRAME RADOME"
G. Fretz and J. K. Burkley, Goodyear Aircraft Co.

10:15 "METAL-TO-METAL ADHESIVE FAILURE AS A FUNCTION OF LOADING RATE"
M. Silberberg and R. E. Supnik, Plas-Tech Equip. Corp.

10:45 Intermission

11:00 "REINFORCED PLASTICS IN TRAILER TANK STRUCTURAL DESIGN"
L. J. Hessburg, Stainless & Steel Products Co.

11:30 "LOW DENSITY EPOXY STRUCTURAL MATERIALS"
K. Cressy, Furane Plastics

12:00 LUNCHEON—*Chairman, Jack Fuller, Chemtrol Div., Rexall Drug & Chem. Co.*
Introduction of SPE President, Frederick C. Sutro, Jr.
Speaker: Lewis Larmore, Ph.D., Senior Consultant on Scientific Research, Lockheed Corporate Group

### AFTERNOON—JOINT SESSION ON MISCELLANEOUS SUBJECTS

*Moderator: Samuel S. Oleesky, Zenith Plastics Co.*

2:00 "PLASTICS IN THE 'ELECTRA'"
Robert Routt, Lockheed Aircraft Corp.

2:45 "OBSERVATIONS ON BEHAVIOR OF PLASTICS AND REFRACTORY CERAMICS IN HIGH TEMPERATURE GAS STREAMS"
Andrew M. Stein and J. P. Sterry, Boeing Airplane Co.

3:15 "NEW DEVELOPMENTS IN ADHESIVES AND SEALERS"
John C. Middleton, Minnesota Mining and Manufacturing Company

### 3:45 OPEN FORUM DISCUSSION

**Committee for First NATEC in Los Angeles.** Front row, left to right: Walter Kadlec, Registration; Don Hamilton, Advisory; Raymond Seymour, Vice Chairman; Jack Fuller, Chairman; Howard Malby, Arrangements; Samuel Oleesky, Program; Robert Steinman, Treasurer; Louis Tallman, Speakers. Back row, left to right: Paul Metzger, House; Thomas Schaub, Printing; Rod Maybee, Reception; Harold Kotkin, Secretary; C. R. Lindegren, Tickets; John Joyce, Publicity; Milton Buck, Visual Aids; William Dewar, Advisory; Charles Zimmerman, Membership.

# NATEC Abstracts

## NATEC • • • • • • • • • • Abstract

### Polypropylene: Properties and Processing

BY W. L. DUNKEL AND WESTLUND, JR., ENJAY COMPANY

Articles fabricated from polypropylene possess a unique combination of lightness, high heat resistance, absence of stress cracking, good mechanical properties, chemical resistance and attractive finished appearance. This combination of properties makes polyproplyene suitable in the fields of injection molding, film, vacuum forming and monofilaments.

From the processor's point of view these desirable properties must be balanced by ease of processing in conventional equipment. This paper discusses their effects on both processability and finished article properties.

## NATEC • • • • • • • • • • Abstract

### Baker PL-11—A New Thermoplastic Polymer

BY DR. C. H. SCHRAM, J. T. BAKER CHEMICAL COMPANY

A new acrylic-type plastic, Baker PL-11, has been developed which is a clear, transparent thermoplastic material possessing a heat distortion temperature of 252°F. (A.S.T.M. Test). This new resin has excellent outdoor weatherability. It can be injection and compression molded and extruded. Moldings made from the polymer are mechanically stable and retain their shape at temperatures up to 250°F. Prolonged exposure to boiling water does not affect the transparency or physical properties of the plastic. Injection molded samples of this material have been subjected to steam sterilization at 10-15 pounds of pressure without loss of transparency or shape.

PL-11 has been processed by almost every technique used on thermoplastic polymers. In general, the technology involved in handling this material closely approximates that of the methyl methacrylate resins currently available. The chemistry of the new polymer will be discussed.

## NATEC • • • • • • • • • • Abstract

### Epoxy Molding Compounds—New Fields for Molders

PAUL E. FINA, FIBERITE CORP.

Epoxy molding compounds promise to be a boon to thermoset molders. Some of the advantages they offer are: Good dimensional stability under all conditions, low molding pressures, (50 psi), retention of electrical properties under rigorous conditions, retention of mechanical properties, exceptional resistance to caustic soda, and continuous heat resistance of 500°F. Another big advantage: epoxies promise to bring lower mold costs. Pin breakage problems are nil. Delicate inserts, tiny pin holes, and molded encapsulation, can be molded in with ease. Molding techniques approximate the phenolics with the exception of molding pressure.

## NATEC • • • • • • • • • • Abstract

### Increasing Plasticating Capacities of Injection Molding Machines

BY DON PETERS AND J. N. SCOTT, PHILLIPS CHEMICAL COMPANY

A new development in nozzle design results in markedly increased plasticating and material temperature uniformity. This device is constructed to restrain low temperature resin in a cross section that is readily heated while allowing higher temperature resin to flow freely into the mold. Use of this new nozzle has permitted production rates of up to five times those obtained with conventional equipment. For example, the maximum plasticating capacity of a three-ounce machine was increased from less than 10 to greater than 45 lbs./hr. The greater melt temperature uniformity resulting from use of this nozzle is evident in much higher quality molded parts. The simplicity in design allows this nozzle to be fabricated in any machine shop at a low cost.

## NATEC • • • • • • • • • • Abstract

### Injection Blow Molding

BY DON PETERS, DAN PERRY, AND J. N. SCOTT, PHILLIPS CHEMICAL COMPANY

This paper describes a low cost blow molding attachment for conventional injection molding machines and discusses this technique for producing hollow items. This method and equipment is very attractive for the production of rigid polyethylene industrial items, toys and housewares. Small lot orders of bottles are economically produced by this technique. Figures showing design, operation and product are included.

## NATEC • • • • • • • • • • Abstract

### Structural Filament-Wound Pre-Pregs

BY L. J. GEIGER, AMERCOAT CORPORATION

This paper will cover recent developments and applications of filament-wound reinforced plastics in the aircraft, missile, and electrical industries, together with a synopsis of applications in other industries. A brief discussion of the development of the filament winding process will be included, and physical properties and strength data will be presented.

A discussion, illustrated by color slides, of a variety of shapes and objects which have been produced will be included, and illustrations of various composite parts and methods will be shown.

In addition, structural filament-wound prepreg as a high strength moldable basic material will be described and illustrated.

Various new thermosetting resins and types of glass and synthetic fibers which can be successfully used with the filament winding process will be discussed.

## NATEC • • • • • • • • • • Abstract

### Amine Boranes and Alkoxy Boroxines as Potential New Curing Agents for Epoxy Resins

BY HENRY LEE AND C. KLOPFENSTEIN, THE EPOXYLITE CORPORATION

Twelve newly synthesized boron compounds were surveyed for use as curing agents, accelerators, or catalysts for curing epoxy resin systems. Amine boranes were found to be latent curing agents, with morpholine borane showing the most promise. Amine boranes were also found to be satisfactory as long pot life accelerators for anhydride cures. Of the other types of boron compounds studied, trimethoxyboroxine, considered as an anhydride, was found to give fast cures at room temperature with numerous types of epoxy resins. Other boron compounds such as alkyl boric acids, borates, and borohydrides did not reveal curing properties. Tests of the various compounds as heat stabilizers were also conducted, but revealed that the volatile nature of the decomposed complexes made them unsatisfactory for this use.

## NATEC • • • • • • • • • • Abstract

### End Uses and Markets by Blow Molding Process

BY T. W. MULLEN, CELANESE CORPORATION

In view of the rapid development of the blow molding process during the last six to eight months, there has been created a need to know as much of the overall picture as possible concerning this method of fabrication. Plastic molders throughout the country are seriously investigating this process and are attempting to obtain as much data as possible on equipment, potential end uses and markets. The object of this paper is to present the manner in which the blow molding process can be applied to four major end use areas and their potential markets. These four are: toys, housewares, industrial items and containers. It will also show how each field has special needs and requirements concerning equipment, product design and material. A description of the items in each field and an estimated market potential will help to present the overall picture. Slides, as well as samples from each category will assist in presenting this paper.

## NATEC • • • • • • • • • • Abstract

### Fluidized Bed Coatings

BY JOHN DELMONTE AND WOODY CRANK, FURANE PLASTICS INC.

The subject of fluidized bed coatings is reviewed with particular emphasis upon application techniques and material selection. Recent developments indicate that there will be considerable interest in the application of powder coatings to metal components.

The development of thermoplastic and thermosetting material formulations for fluidized bed coatings are reviewed, and possibilities outlined for expanding this important technique.

Design features, advantages and disadvantages of this new method of applying plastic coatings from plastic powders are reviewed.

## NATEC • • • • • • • • • • Abstract

### Laboratory and Field Evaluation of Plastic Piping Systems

BY MARTIN USAB, CHEMTROL

This paper deals with the methods for developing comprehensive data for the application of plastic materials in piping systems and auxiliary equipment. The paper points out the unique behavior of plastic in piping systems and demonstrates the necessity of a unique approach to studies of such properties as Creep, Thermal Expansion, Chemical and Thermal Degradation, as well as special coupling and fabrication techniques.

## NATEC • • • • • • • • • • Abstract

### Design, Fabrication and Erection of the 110-foot Diameter Space Frame Radome

BY GEORGE FRETZ AND J. K. BURKLEY, GOODYEAR AIRCRAFT CORPORATION

This paper will cover all phases of effort from concept to erection to produce a radome fulfilling the electrical and structural requirements of the LAR system for Nike-Zeus.

The schedule of efficient design will be followed and the evolution of a structural and electrical compatible configuration will be demonstrated for these particular requirements. This same schedule of concept investigation is suitable for any radome design.

In addition to illustrations of design and stress work the demonstration of electrical performance by scale models tested on the antenna range will be shown. After the radome design was complete it was necessary to design and build a laminating press which would make a single seamless sheet 14 foot by 22 foot. This and the entire laminating process will be shown.

At erection site the importance of having a proper base will be vividly displayed.

## NATEC • • • • • • • • • • Abstract

### Metal-to-Metal Adhesive Failure as a Function of Loading Rate

BY M. SILBERBERG AND R. H. SUPNIK, PLAS-TECH EQUIPMENT CORPORATION

A study of lap-shear performance of a number of adhesive systems at varying temperatures will be reported over a range of testing speeds of from 0.02 inches/minute (obtained via an Instron Model TT-C Universal Tester) to 2,000-4,000 inches/minute (obtained via a Plastechon Model 581 Universal Tester). Both room temperature and elevated temperature performance will be examined for adhesive systems including Shell 422, Eastman 901, and others. The data to be presented are felt to be of particular importance since in-service failure of adhesive joints is so often associated with both temperatures other than room and load application which verges upon the shock loading domain.

## NATEC • • • • • • • • • • Abstract

### Reinforced Plastics in Trailer Tank Structural Design

BY L. J. HESSBURG, STAINLESS & STEEL PRODUCTS CO.

Stress cracking of thin-walled tanks is an all too common occurrence. The most common method of tank reinforcement is to apply steel encircling rings of channel or hat section shape. A large tank may contain 500-1000 lbs. of such reinforcement, and circumstances may also require that they be welded to the shell, at great cost in welding, grinding and polishing time.

To reduce both weight and labor time, we have developed a system for applying fibreglass-reinforced plastic rings, cured in place. We employ a pre-impregnated, pre-oriented material (Minnesota Mining & Mfg. Co.'s "SCOTCHPLY") with epoxy impregnant for maximum adhesion. The design virtuosity available with such a material is great indeed. With it we can tailor the size, shape and thickness of supports to the individual problem with essentially no mold cost, using a simple vacuum bag forming technique. The material is almost perfectly elastic to its very high ultimate strength, it has directional properties, excellent fatigue strength, and is quite flexible.

## NATEC • • • • • • • • • • Abstract

### Low Density Epoxy Structural Materials

BY KENNETH CRESSY, FURANE PLASTICS, INCORPORATED

A series of epoxy resin formulations are now available which give the plastics industry a new type of lightweight material. By combining one or more of a variety of new fillers with standard epoxy, hardener systems, a syntactic foam-like material is produced with a specific gravity of 0.6 yet with strength properties comparable to those of a filled epoxy of two or three times the weight. A formulation of this type would be a pourable, casting resin readily adapted to filling irregular shapes in structures where weight must be limited but strength retained.

Other epoxy formulations have been produced with specific gravities of about 0.3 or 20 pounds per cubic foot. These are paste-like or relatively dry mixtures which may be troweled or tamped into place before curing. The applications of these lightweight epoxies are indicated by their excellent physical and electrical properties. This paper will discuss the physical property data for the interest of the design engineer.

## NATEC • • • • • • • • • • Abstract

### New Developments in Adhesives and Sealers

BY J. C. MIDDLETON, MINNESOTA MINING AND MANUFACTURING COMPANY

Our present challenge in the development of new adhesives and sealer lies in the areas of resistance to temperatures up to 1000°F for sustained periods of time—providing materials with structural strengths when bonded to relatively inert surfaces—resistance to the effects of high energy fuels—new bond techniques—good dielectric properties—to name only a few.

Recent developments in polymer research have provided complex structures that hold considerable promise to solve these problems.

Adhesives in film form have recently become available for performance in the 500°F range with heat resistant steels. Others have been engineered to provide reduced interference to radar transmission.

New polymers have also been incorporated into sealing materials that are resistant to combinations of fuels and heat.

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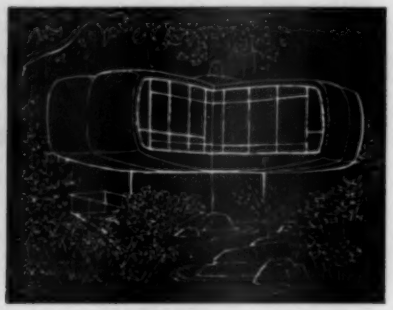
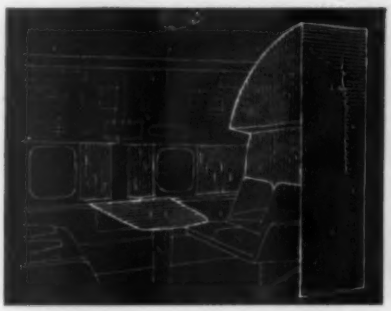
**The success of products containing Douglas *Aircomb* has resulted in a great expansion of its use by plastics manufacturers. Aircomb possesses the desirable combination of high strength and rigidity, light weight, good insulation and acoustical characteristics, resistance to corrosion and virtual elimination of maintenance. Faced with glass laminates or plastics, *Aircomb* products provide both structural and decorative advantages.**

**...IN BOATS** – (meets Bushipe spec. MIL-H-21040) More than 50 U.S. and foreign boat manufacturers are using *Aircomb* for hull reinforcement, decks, partitions, seats, and topside structures. Bumpers of *Aircomb* are also being employed as shock-absorbing cushions in special marine launching operations.

**...IN SPECIALTIES** – Hundreds of thousands of pounds of unimpregnated Douglas honeycomb are being sold yearly to specialty manufacturers. Now available in a variety of colors, it is being used for sport hats, lamp shades, flower vases, miniature Christmas trees, coasters, and in hundreds of other interesting ways.

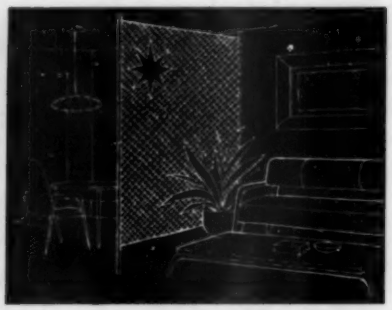


**...IN MODERN BUILDINGS** – *Aircomb* is a primary structural element in the famous "Monsanto House of the Future" now on display in Disneyland, California. It is being used in many new buildings for both exterior and interior applications like curtain walls, partitions, ceilings, floors, decorative panels, etc.

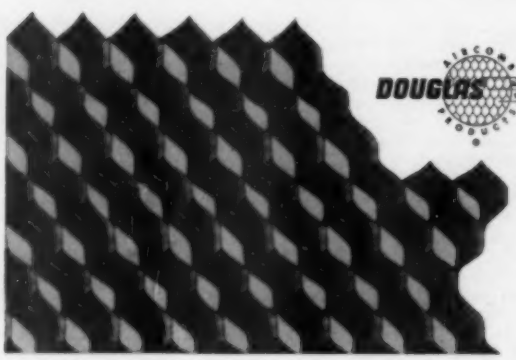


**...IN AIRCRAFT** – *Aircomb* is widely used in modern airliners like the Douglas DC-8 jetliner for tables, partitions, shelves, cabinets and for exterior access doors. Used for aircraft tooling faced with glass laminates, it is less affected dimensionally by moisture or temperature changes than any other material and can hold extremely close tolerances.

**...IN MILITARY APPLICATIONS** – Faced with glass laminates, *Aircomb* roofs for electronic and radar trailers are capable of bearing a distributed load of up to *1000 lbs.* per square foot. Treated acoustically in walls, it is superior to all other known materials for sound insulation. *Aircomb* is also being used in ground support equipment of all types.



**...IN DECORATIVE APPLICATIONS** – Room dividers made of *Aircomb* sandwiched between translucent, transparent or opaque facing materials are being used where the combination of beauty, light weight, rigidity and durability are required. The symmetrical pattern of the *Aircomb* provides a pleasing effect increasingly in demand by decorators.



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# Section News

*Chicago*

## Change in Directors

HARRY E. BENNETT

At the June meeting the Board of Directors accepted the resignation of Joe Gits, Jr. Because of the activity involved in heading up his relatively new company and the lack of time for other affairs, Mr. Gits felt this action best, and the Board regretfully accepted. Ben Brown, Hercules Powder Co., will fill the unexpired portion of Mr. Gits' term. Mr. Brown will be Editor of Chicago Section's Newsletter.

*North Texas*

## Plastic Pipe Engineering

DAVID A. DANIELS

Section member, Ray Perkins, Director of Technical Services for Southwestern Plastic Pipe Co., Mineral Wells, spoke on plastic pipe engineering during the July meeting.

The monthly Board meeting was held in the Board Room of Hurst State Bank in Hurst, and it was announced that Hubert Poskey has resigned as treasurer and D.C. Novelli of Convair has taken over. Mr. Novelli will serve as Chairman of the National Technical Conference to be held by the Southwest Society of Aircraft Materials and Process Engineers to be held at the Hotel Texas on December 8th and 9th. Held in Fort Worth, it will be called the "National Aerospace Symposium." At that time it is expected that the Southwest Section will make a bid for establishment of national headquarters in the Dallas-Fort Worth area.

*We're Sorry*

Our apologies to MARIO J. PETRETTI, SPE Past President and National Councilman representing Southeastern Ohio Section, whose name was inadvertently omitted from the list of Distinguished Members, published in the Membership Roster, August 1959 SPE Journal.

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# Technical Conferences

## RETEC

## Plastics in the Shoe Industry

*Sponsored by the St. Louis Section*
*of the Society of Plastics Engineers*
*November 4, 1959, Hotel Statler, St. Louis, Mo.*

**PURPOSE**

Objective of the symposium is technical discussions of latest plastic materials, applications and manufacturing processes in the shoe industry. Originally, material in shoes was leather. The discussions cover plastic materials which provide a more suitable material at lower cost and also cover features to prevent misapplication of plastics.

**PROGRAM**

**Nov. 3, 1959**

Daniel Boone Room—7:00 PM

**Pre-Conference Dinner and Meeting**

National Officers and Board of Directors of St. Louis Section (all members and guests invited). Please notify Registration Committee if you desire to attend.

**Nov. 4, 1959**

**Morning Session**

9:00 AM—12:00 Noon
*Chris Kacalieff—Moderator,*
*(Chris Kaye Plastics Mfg. Co.)*

9:00 AM—Ballroom

Opening of Conference, Otto Wulfert, General Chairman

LABORATORY TESTS FOR PLASTIC HEELS

J. R. Szumski (speaker), E. E. Joiner, and F. J. McGarry, Fred W. Mears Heel Co., Inc., Lawrence, Mass.

A series of tests are described for the evaluation and control of production of plastic heels for women's shoes. An impact, flexing and nailability test is described.

INJECTION ON SOLE MOLDING

T. E. Daly, United Shoe Machinery Corp., Research Div., Beverly, Mass.

This paper describes an injection molding process for applying PVC soling compounds onto the bottoms of leather upper shoes. Sound film will show equipment in operation.

MOLDS FOR PLASTIC SHOE COMPONENTS

Amelio J. Cocci, Standard Tool Co., Leominster, Mass.

Paper will describe the building of molds for the component parts of shoes such as molds for heels, Dutchman, inner soles, top lifts, shoe counters, shoe lace ornaments and buckles, and supports.

URETHANE POLYMERS IN THE SHOE INDUSTRY

G. A. Baseden, E. I. du Pont de Nemours & Co., Inc. Elastomers Laboratory, Wilmington, Del.

Urethane polymers have a combination of physical characteristics and versatility of application methods which suggest their use in the shoe industry. Elastomers, coatings, binders, and foams produced from urethane systems exhibit high strength and load bearing capacity.

VINYL COATED FABRICS FOR THE SHOE INDUSTRY

E. G. Hamway, Director of Research, The General Tire and Rubber Co., Textileather Div., Toledo, Ohio

Since 1940, vinyls have become commercially available.

1) Linings
   a) Vinyl coated rubber saturated flannels, non-woven fabrics, and vinyl coated papers.
2) Uppers
   a) Vinyl coated sateens—generally combined.

**12:00-2:00—Luncheon**

Introduction of Frederick C. Sutro, Jr., SPE National President.

PLASTICS IN THE SHOE INDUSTRY

R. H. Richards, International Shoe Co., St. Louis, Mo.

This presentation gives a basis for judging comparative merits of plastics and leather as used in the shoe industry. Contrasts are drawn between the raw materials, the economics, and the finished characteristics of leather and plastics.

**Afternoon Session**

2:00 PM—4:00 PM

*Pete Coons—Moderator, (Dow Chemical Company)*

AUTOMATIC EXTRUSION MOLDING OF SHOE COMPONENTS

Gordon Cooper, International Vulcanizing Corp., Boston, Mass.

The operation of the Foster-Wucher FW 700 machine will be described in relation to the injection molding of all PVC sandals, to the molding of PVC insert molded outsoles and heels and to a shoe process for the direct sole molding of PVC compounds to all types of footwear. A sound film shows the machines in operation.

FACTORS AFFECTING INJECTION MOLDED POLYETHYLENE SHOE COUNTER PERFORMANCE

S. R. Melvin, Technical Service, Polyethylene Monsanto Chemical Co., Plastics Division, Springfield, Mass.

The effects of polyethylene melt index, density, and processing conditions upon injection molded shoe counter performance are outlined. Injection molding theory and practice as applying to the production of counters is discussed. Counter uniformity and quality are examined in terms of the variables of resin type and molding conditions. Shrinkage, warpage, residual molded stress level, stress cracking, rigidity, and flex life are presented, with suggestions for organization of local quality control tests. Several field case histories are presented.

PORON INSOLE

Benjamin B. Levy
Rogers Corporation, Rogers, Conn.

A. Background of Leather
B. Discussion of Foot Comfort
C. Introduction to Poron
D. Description to Manufacturing Processes
E. Theory Behind the Poron Insoles
F. Results of Wear Tests
G. Explanation and Demonstration of Moisture Transmission, Wicking Action, and Porosity with Graphs and Equipment Demonstrating Points.
H. Physical Properties of Poron
I. Other Uses of Poron

FOAMED PLASTICS

Armand G. Winfield, Plastics Product Development, And Design Engineer, DeBell and Richardson, Inc Hazardville, Connecticut

The paper will deal with several aspects of shoe decoration including:

1. Plastic Coatings, Plastic Cover Fabrics, Molded and/or Embedded Heels, Molded and/or Embedded Buttons, Bows or other Decorations.
2. The one-piece molded shoe (plastisol or sintered polyethylene) and its far reaching effects on total shoe designing.
3. New concepts in shoe design.

**PANEL DISCUSSION**

Moderators:

Dick Koehrman—Harold Kalde
Co-Chairmen Program Committee

Members of the panel will be engineers and representatives of the plastic and shoe industries. Speakers for morning and afternoon sessions will be present for discussion of subjects not possible to cover during session. Sufficient time will be available for private discussions and requests for information not available at conference.

## About Members

**Edwin A. Brown** has been appointed general manager of Industrial Research Laboratories, division of Honolulu Oil Corp. Mr. Brown joined the firm in 1937 and was formerly manager of engineering and production. He is a member of the A.S.M. and a senior member of the Southern California Section of SPE.

**William A. Dunlap,** an affiliate of the Southern Texas Section of SPE, has been advanced to manager of the Dow Chemical Company's plastics technical service activities in the South. Mr. Dunlap will be in charge of a group of specialists who assist plastics designers and manufacturers in selecting the proper plastic and fabricating process for production of a given product. The group also provides follow-up customer service in solving production and other technical problems. Mr. Dunlap joined Dow in 1951 at Midland headquarters. He earned a B.S. degree in chemistry from Purdue University.

**Max M. Lee,** who was formerly associated with the National Bureau of Standards, Washington, D. C., and more recently with the General Electric Co., Fort Wayne, Indiana, is now operating as an independent chemical and engineering consultant with offices at 1023 West Sherwood, Fort Wayne, Indiana. Mr. Lee, who is National Councilman representing the Northern Indiana Section of SPE, will specialize in insulation materials and process development for the electrical and electronic industries.

**William P. Hayes** and **C. W. Kufner** have filled new positions at Nosco Plastics, Inc., Erie, Pa. Mr. Hayes has been named to fill the newly created position of production superintendent, and Mr. Kufner was appointed plant manager. Mr. Hayes joined Nosco 18 years ago as a press operator. He had advanced to the position of molding superintendent before his latest promotion. Mr. Kufner had formerly been general superintendent prior to his new position. Both are members of the Northwest Pennsylvania Section of SPE.

**Allan G. Serle,** current president of the SPE Newark Section, has joined the Molding and Extrusion Technical Service Group of the Celanese Corp., at its Technical Service and Application Laboratory in Newark. A native New Yorker, Mr. Serle attended Brooklyn College and received a B.M.E. degree from the CCNY School of Technology in N. Y. in 1950. He held the position of Production Engineer at the Tech-Art Plastics Co. in Morristown, N. J. from 1950 to 1954, and until recently, was Senior Product Engineer of the Shaw Insulator Co. in Irvington.

Serving for three years as Chairman of the SPE Newark Section's Education Committee, Mr. Serle participated in the foundation of the Plastics Engineering Technology Program now offered at the Newark College of Engineering, and has himself, since 1954, conducted a class in "Compression and Transfer Molding," one of the courses in the program. In November of 1958, the Newark College of Engineering presented him with a certificate "in recognition of his contributions to the advancement of education in the field of

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plastics technology and in appreciation of the valuable assistance he has rendered to the college as an advisor, consultant and instructor for the Special Courses Division's program of plastic courses."

**Dr. K. O. William Sandberg** has been appointed to the position of executive vice president of Norton Laboratories, Inc., Lockport, N. Y. Dr. Sandberg comes to Norton from the plastic division of the General Electric Co., where he served as engineering manager for all plants of the General Electric plastics department. He was a contributing author of the McGraw-Hill Handbook on Industrial Engineering. He is a recognized authority on multiple machine operations for factories. Dr. Sandberg was an International American Delegate to the Seventh Annual World Management Congress at Stockholm. He is a graduate of Columbia University and N. Y. University and holds a degree of Doctor of Engineering Science. He is a member of the Chicago Section of SPE.

**Richard E. Mortberg** was appointed sales representative for Diamond Alkali Company's plastics division in the Chicago area. Mr. Mortberg joined the Diamond organization after having been employed by Dupont for five years. He is a graduate of the University of Massachusetts, where he earned his B.S. degree in chemistry in 1954. Then, enrolled at the University of Delaware, he pursued extension courses for two years. A member of the Philadelphia Section of SPE, and the SPI, he holds membership in the ACS and the ASTM.

**Edward C. Richardson** has been appointed Chicago division sales manager for U.S.I. Mr. Richardson, who holds a Bachelor of Chemistry degree from Cornell University, has been with U.S.I. since 1940 and was Boston division sales manager for the company from 1950 until the time of his new appointment. He is a past president of the Chemical Club of New England and also is a member of the Eastern New England Section of SPE and also of the SPI.

**Louis R. Wanner** was named chief engineer of Sylvania's Parts Division, a newly created post. Mr. Wanner has been manufacturing manager in charge of metal base and plastics operations for the division since 1957. He joined the Sylvania organization in 1948, as a senior engineer. In 1950, he was appointed plant manager of plastics operations, a position he held until 1957. He attended Lehigh University, where he received a B.S. degree in electrical engineering. He has also done graduate work at the University of Pennsylvania in Phila. An author of several articles on the plastics industry, he is a member of IRE, AIEE, Philadelphia Section of SPE, and the 08C Socket Committee of RETMA.

Dr. K. O. William Sandberg

Edward C. Richardson

# RETEC

# Technical Conferences

## Plastic Finishing

**Sponsored by the Buffalo Section in cooperation with the Plastic Finishing Professional Activity Group. Friday, October 16, 1959. Hotel Niagara — Niagara Falls, N. Y.**

### PURPOSE

A large percentage of all molded plastics must be finished or decorated in one way or another before the product is ready for the market. The purpose of this conference is to cover in one program the more important methods by which this phase of the plastic industry can best be accomplished.

### PROGRAM

1. Finisihing and Decorating of Plastic Materials by Silk Screening, Printing, and Spray Masking
   —Arthur Skeels, Sr.—Art Decorating Co., North Bergen, N. J.
2. New Development in Coatings and Vacuum Metallizing Systems for Plastics.
   —T. E. Hayden—Bee Chemical Company, Chicago, Illinois
3. Hot Leaf Stamping
   —Martin A. Olsen—Olsenmark Corp., New York, N. Y.
4. Mechanical Finisihing of Plastics Using Coated Abrasives
   —Ronald Reid—Carborundum Co., Niagara Falls, N. Y.
5. Luncheon Speaker—Peter W. Simmons, 1957 SPE National President—Progress in Goals of National Society—Second Luncheon Speaker to be announced.

Three papers will be presented in the morning and the fourth after the luncheon in the afternoon. The last talk will be followed by a discussion period in which the four speakers will form a panel.

**Committee members:**

*Honorary Chairman*—H. S. Nathan (National Treasurer)
*General Chairman*—K. L. Ditzel
*Program Chairman and Moderator*—G. K. Storin
*Treasurer*—A. A. Engl
*Registration and House Chairman*—J. Henderson

**Registration Fee**—$7.00 (includes luncheon and preprints)

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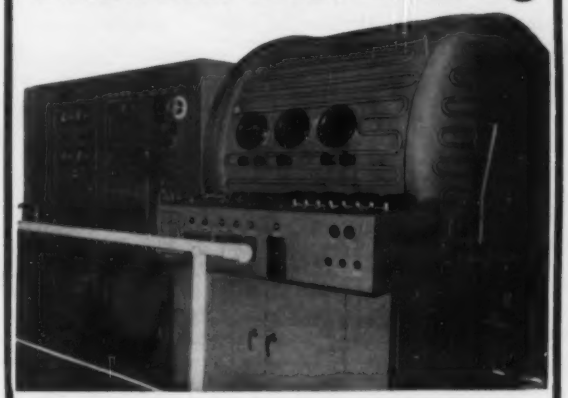

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# Technical Meetings Calendar

## 16TH ANTEC

ANNUAL TECHNICAL CONFERENCE—January 12-15, 1960, The Conrad Hilton, Chicago, Ill. Sponsored by the Chicago Section. For more information, contact General Chairman Franklin L. Fine, Rohm & Haas Co., 5750 W. Jarvis Ave., Chicago 31, Ill. Request for papers on page 275 of the April SPE Journal.

## 1959 NATEC

NATIONAL TECHNICAL CONFERENCE—October 13-14, 1959. The Ambassador, Los Angeles, Calif. For more information, contact General Chairman, Jack C. Fuller, c/o Chemtrol Co. 10872 Stanford Ave., Lynwood, Calif. See program and abstracts page 815, this issue.

## RETECS

VINYLS—October 7, 1959, Cleveland Engineering Society, 3100 Chester Ave., Cleveland, Ohio. Partial program page 745, August SPE Journal. For further information contact Jack R. Pecktal, 13212 Shaker Square, Cleveland 20, Ohio.

PLASTICS FINISHING—October 16, 1959, The Niagara Hotel, Niagara Falls, N. Y. Sponsored by the Buffalo Section in cooperation with the Plastics Finishing PAG. For program, see page 823, this issue. Chairman Gordon K. Storin, 3 Forest Rd., Lewiston Heights, Lewiston, N. Y.

PLASTICS IN THE SHOE INDUSTRY—November 4, 1959, Statler Hotel, St. Louis, Mo. Sponsored by the St. Louis Section. For program information, see page 820, this issue. Otto Wulfert, Chairman, c/o Wagner Electric Co., 6400 Plymouth Ave., St. Louis 14, Mo.

PLASTICS IN PACKAGING—November 19, 1959, Berkeley, Calif. Sponsored by the Golden Gate Section. For information write to Chairman Frank D. Allen, L. H. Butcher Co., 15th & Vermont Sts., San Francisco 1, Calif.

STABILITY OF PLASTICS—December 1, 1959, National Academy of Science Bldg., 2101 Constitution Ave., NW., Washington, D. C. Sponsored by the Baltimore-Washington Section. For information write to Chairman Myron G. DeFries, Atlantic Research Corp., Alexandria, Va.

## — SECTION MEETINGS —

QUEBEC—September 18, 1959. Golf Outing to be held at Granby P. Q.

GOLDEN GATE—September 24, 1959. Tour of the Reichhold Chemical plant. Dinner location to be announced.

NORTHWESTERN PENNSYLVANIA—September 24, 1959. First Fall meeting at the Erie Eagle's Club, 6:30 PM. Speaker will be from the Technical Department of Celanese Corporation. Subject: Blow Molding.

AKRON—September 28, 1959. First Fall meeting. Dinner and talk, "Extrusion of Plastic Materials," by Al Kaufman, Prodex Corp., to be held at Akron University Club.

CENTRAL INDIANA—September 29, 1959. Ladies Night and a color film, "House of the Future." Talk to be given by T. J. Martin, Monsanto Chemical Co.

## —EXTRUSION WORKSHOP—

CENTRAL OHIO—Third Extrusion Workshop sponsored in cooperation with the Extrusion PAG.

**Date:** October 20, 21, 1959

**Place:** Ohio State University, Ohio Union Conference Theater

**Fee:** $35.00 to include registration, 2 lunches, dinner and coffee.

**Speakers:** E. Veazey, Dow Chemical, E. Bernhardt and H. Kessler, The Du Pont Co., B. Maddock, Union Carbide Plastics Co., F. Nissel, Prodex Corp., M. Underwood, Monsanto Chemical Co., and R. Sackett, Hartig Extruders. (Moderator)

**Attendance:** Anyone from any Section may attend.

**Registration:** Send fee, name, address and company affiliation to Chairman Mr. Robert O. Zimmerman, Plastex Co., 3232 Cleveland Ave., Columbus, Ohio. Deadline is September 30, 1959

## New Tour Speaker Available for 1959-60

The latest addition to the Speakers' Subcommittee, Meetings Committee, is Mr. E. E. Ziegler, Dow Chemical Co. As a tour speaker, Mr. Ziegler will touch upon one of the fastest growing areas of the plastics industry—plastics in the building industry. He will describe the use of plastics in foundations, superstructures, roofs, illumination, and decoration. Colored slides will be used to illustrate this entire discussion.

Mr. Ziegler graduated with honors from Wayne University with a B.S. degree in Mechanical Engineering. Prior to joining Dow Chemical Co., he was with General Motors Truck for 3½ years, and Standard Oil Co., also 3½ years. He joined The Dow Chemical Co. in 1943 and is presently serving as Manager of Fabricated Products Group in Plastics Technical Service.

E. E. Ziegler

Any section desiring to schedule Mr. Ziegler should write or phone Mr. John A. Picard, Plastics Technical Service, The Dow Chemical Co., Midland, Mich.

## The Society of the Plastics Industry, Inc., Announces Coming Events

**October 1, 2**—Fifteenth New England Section Conference at Wentworth-by-the-Sea, Portsmouth, N. H.

**February 2, 3, 4**—Fifteenth SPI Reinforced Plastics Division Conference, Edgewater Beach Hotel, Chicago, Ill.

**April 25, 26**—Eighteenth Annual SPI Canadian Section Conference, London Hotel, London, Ont., Canada

**May 7-13**—SPI National Conference and Annual Meeting, Cruise on "Queen of Bermuda."

## London Conference on Plastics in Building

The Plastics Institute, London, England, will hold a conference on "The Influence of Plastics in Building". Dates: Nov. 19 and 20, 1959. Registration forms available from the Secretary, the Plastics Institute, 6 Mandeville Place, London, W. 1.

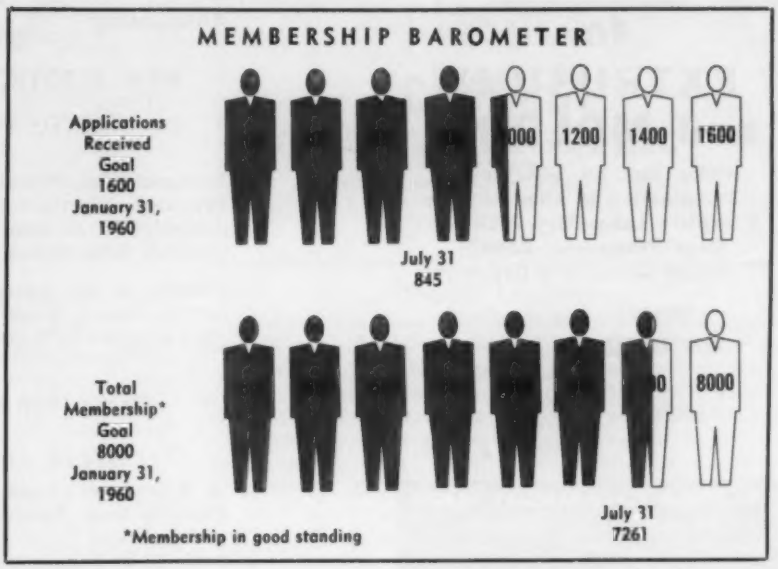
# Book Reviews

### The Chemistry of Industrial Toxicology

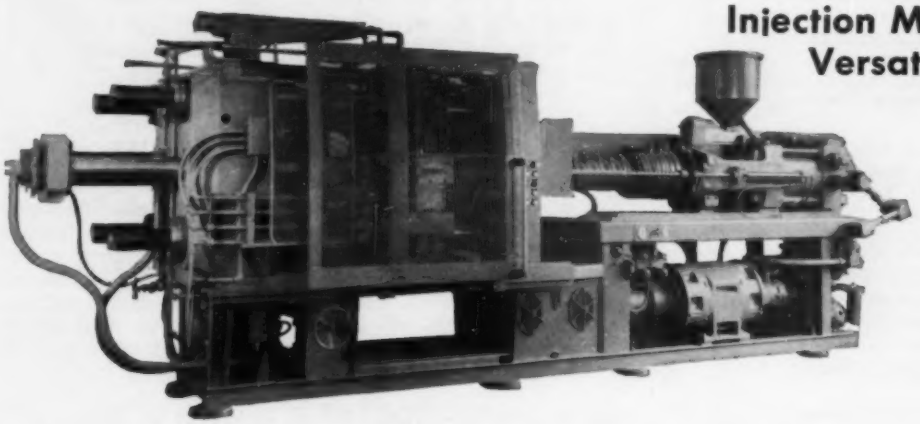
**Hervey B. Elkins (John Wiley & Sons, Inc., New York 1959, 2nd edition, 452 pp., $11.50)**
This edition is enlarged and brought up to date on fields of recent expansion, such as insecticides and radioisotopes. The chemical aspect of industrial toxicology treated here will appeal more to plastic chemists and engineers than books on physiological or medical toxicology, which require a different background and training. Furthermore, this manual seems to contain every kind of information needed, from metals to organic chemistry, from solids to gases, from detection and analyses to allowed concentrations.

There are very comprehensive tables, easy to read, giving the hazardous concentrations of solvents, plasticizers and other chemicals involved in plastics mixing, molding, laminating and other current manufacturing operations. Other tables give the maximum allowed concentrations of chemicals used every day in the plastics and allied industries. As you won't forget the requirements of the Food Additives Law in its last month of grace, this is one more reason for you to buy this excellent manual.

*Dr. Louis C. Barail*
*Barail Associates*







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## BOOK REVIEWS

### Chemistry Made Easy

**Cornelia T. Snell and Foster D. Snell (Chemical Publishing Co., Inc., New York 1959, 196 + 239 + 262 pp., $10.00)**

In 1943, this well known husband-and-wife team of chemists published 4 booklets for the beginner in chemistry. 16 years later, they have revised and enlarged three of these volumes and published them under a single cover.

The three parts still have their own pagination as seen above. The first one deals with generalities on the elements, electrochemistry, acids, alkalies and pH. The second part is devoted to non-organic chemistry, colloids and radioactive elements. In the third part, the reader finds organic chemistry, vitamins and antibiotics. The claim contained in the title is justified; this book is easy to read and even a seasoned chemist might glance at it, if only because it will remind him of his first dealings with chemistry.

*Dr. Louis C. Barail*
*Barail Associates*

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## NEW ELECTRONIC & AUTOMOTIVE RETEC PREPRINT BOOKS

**Encapsulation, Printed Circuits, and Fluidized Bed Processes**—Northern Indiana Section, 15 of 23 papers presented. $3.00 members; $4.50 non-members. (See program SPE Journal, April, 1959, p. 319).

**Plastics in the Automotive Industry**—Detroit Section, 4 papers, $2.00 members; $3.00 non-members. (See program SPE Journal, May, 1959, p. 443).

## Other 1959 RETEC Preprint Books

BOATS, AIRCRAFT & MISSILES

★ **A Designer's Look at Reinforced Plastics from the Pleasure Boat, Aircraft and Missile Industries Viewpoint**—North Texas Section, 6 papers. $2.00 members; $3.00 non-members. (See program SPE Journal, April, 1959, p. 324).

METALS INDUSTRIES

★ **Plastics in the Metals Industries**—Pittsburgh Section, 10 papers. $3.00 members; $4.50 non-members. (See program SPE Journal, April, 1959, p. 324).

## SPE PLASTICS ENGINEERING SERIES

**Vol. II—Processing of Thermoplastic Materials,** 705 pages. $14.40, members; $18.00, non-members.

**Vol. I—Quality Control for Plastics Engineers.** $3.98, members; $4.95, non-members.

## ANTEC PREPRINT BOOKS

**Vol. V,** 1959, New York City, 96 papers. $7.50, members; $12.50, non-members. Single preprints of individual papers, Vol. V, while they last, $0.25 each, members; $0.40 each, non-members.

**Vol. IV,** 1958, Detroit, 94 papers. $5.00, members; $7.50, non-members.

**Vol. III,** 1957, St. Louis, 60 papers. $5.00, members; $7.50, non-members.

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# Employment & Service Guide

## POSITIONS OPEN

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### Chief Engineer

Well established plastics company in Central New England has an opening for a person who has had at least 2 years experience as a CHIEF ENGINEER and a minimum of 10 years experience in Mold Design, preferably in the toy and novelty line. Extrusion experience helpful. Five figure salary commensurate with experience and background. All replies kept confidential. Please send resume and references. Write Box 5459, SPE Journal, 65 Prospect St., Stamford, Conn.

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B. S. in chemistry or chemical engineering. Experience in all phases of compounding plastisols and organasols essential. Knowledge of adhesives, and general line of polymers applicable to coated fabrics desirable but not necessary. Excellent opportunity for advancement in a medium-sized progressive company. Send detailed resume of background and experience, including salary requirements. All replies will be treated with strict confidence. Reply to: Box 5059, SPE Journal, 65 Prospect St., Stamford, Conn.

### Market Development—Polystyrene

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2. Do you have a B.S. degree?
3. Do you have a "sales" type of personality?
4. Are you interested in an opportunity to grow with a dynamic, youthful organization?

If you can answer *yes* to all 4 of these questions, you may be just the man we're looking for. Write us and send your detailed resume to:

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Employee Relations Coordinator
Amoco Chemicals Corporation
910 South Michigan Avenue
Chicago 80, Illinois

### plastics chemist

Experienced — —
Development and applications testing of additives in all types of Polymers.
Send complete resume including salary requirements to:
GEIGY CHEMICAL CORP.
Saw Mill River Road,
Ardsley, N. Y.

### Plastics Engineer

Mechanical engineer with minimum of five years' experience in processing of thermoplastics. Extrusion experience desirable. Must be able to design equipment, supervise experimental work and analyze data. Technical report writing ability necessary. Please send detailed resume including education, experience and salary requirements to: E. R. Patterson, Employment Manager, Olin Mathieson Chemical Corporation, 125 Munson Street, New Haven, Connecticut.

### Midwest Manufacturers' Representatives Wanted

To sell custom-molded compression, transfer and injection molded plastic components and extruded sheets and shapes to industry on commission basis. Molder is long-established, has 750 employees. Several midwest states open. Applicants should have established territory and industrial accounts. Reply fully to: Box 5159, SPE Journal, 65 Prospect St., Stamford, Conn.

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Good opportunity for plastics engineer with approximately 10 years experience in molding and process work and with good general knowledge of plastics field. Work is on all phases of product and process work with leading New England plastics research and development laboratory. Send resume to Mr. M. Mead.

DeBELL & RICHARDSON, INC.
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### Plastics Extrusion Engineer—M.E., MSME

Seven years' extrusion experience as process engineer in wire and cable manufacture. Responsibilities include knowledge of product development, shop operation and some cable design. Seeking to broaden and improve professionally as technical representative or in a product development position. For full particulars reply to Box 4359, SPE Journal, 65 Prospect St., Stamford, Conn.

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Industrious and imaginative plastics engineer with five years' experience in compound development, production and technical service of thermoplastics desires responsible position with supplier or fabricator. Emphasis on extrusion. Proven ability to estimate markets, generate volume sales. Prefer Northeast. Reply Box 5259, SPE Journal, 65 Prospect St., Stamford, Conn.

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Young, tireless engineer (BS ChE) with two full years of extensive work in plastic and rubber compounds desires position in a sinusitus-free climate—preferably Southwest. Will take responsibility for setting up plastics laboratory for any firm interested in potting electrical circuits, tailoring plastics for end uses, and/or writing of and testing to specifications related to incoming materials or for use as engineering data. Resume on request. Reply Box 5559, SPE Journal, 65 Prospect St., Stamford, Conn.

### Plastics R & D Engineer-Administrator

Over ten years' experience in plastics. Last four and a half in R & D administration. Considerable experience in extrusion, particularly in polyolefins. Also considerable extrusion experience with other plastics. Have good knowledge of calendering, laminating, embossing, heat sealing, and film orientation. Some experience in blow molding. Have worked on process development of both thermoplastic and thermosetting resins. Also on rheological studies of many materials. Some knowledge of market research.

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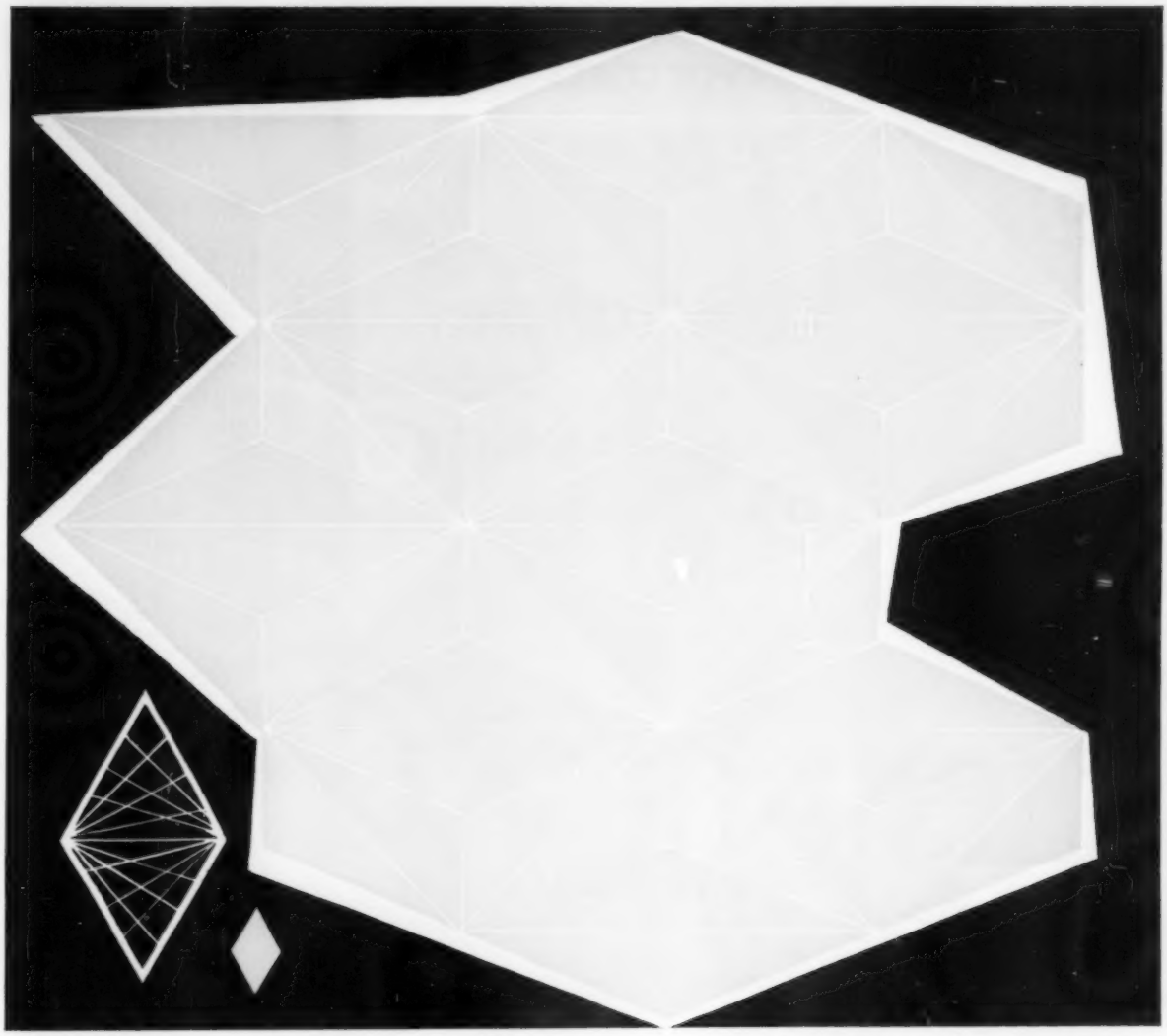

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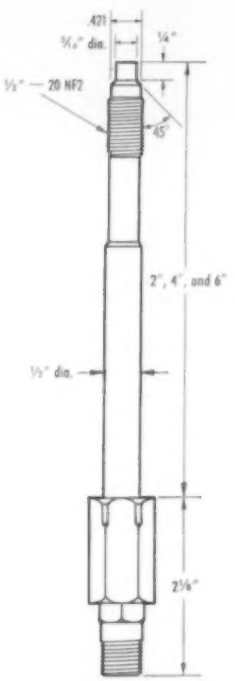


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Norwood Controls transducers with high temperature adaptors have been used for several years in plastic extruder research by leading plastic producers. This experience has now been applied to the development of a transducer designed to fit standard production equipment. It possesses the same high performance characteristics as Norwood's well-known engine pressure pick-ups. Write for full technical data . . . Norwood Controls Unit, Detroit Controls Division, 932 Washington St., Norwood, Mass.

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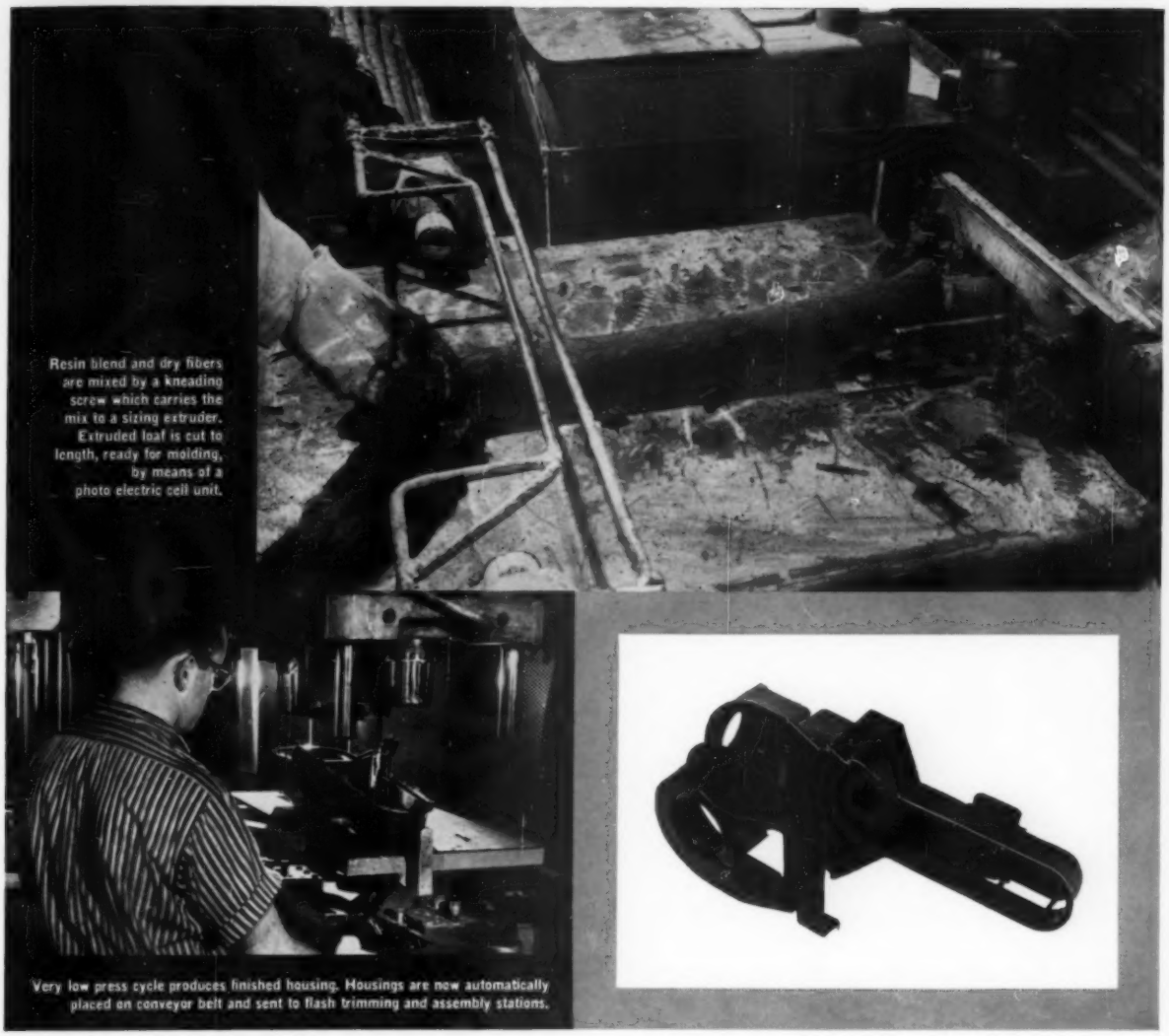

Resin blend and dry fibers are mixed by a kneading screw which carries the mix to a sizing extruder. Extruded loaf is cut to length, ready for molding, by means of a photo electric cell unit.

Very low press cycle produces finished housing. Housings are now automatically placed on conveyor belt and sent to flash trimming and assembly stations.

# Premix moldings speed assembly, make a better heater housing for Ford Motor Company

When you turn to premix moldings for reinforced plastic parts, you benefit from higher quality of product and increased production. The Ford heater housing above is a prime example.

The housings formerly were made of stamped and welded metal. A switch to premix molding eliminated time-consuming assembly problems, produced a better product and increased production rate. Fillets, slots, holes and recesses are formed in the mold, clean-cut and precisely located. Final assembly is quick and easy. Unit costs are lower.

For making reinforced plastic products, premix molding has many advantages. Because the reinforcing fibers are blended with the resin *before* molding, they are uniformly distributed, regardless of wall shape or thickness. This means uniform strength throughout the unit. Preforming is eliminated. So are resin-rich areas, no matter how complex the mold or how heavy the section.

Molders of strong, rigid, reinforced plastic parts have found that premix moldings made with Dow vinyltoluene and Dow styrene have definite manufacturing and product advantages. Production is higher, costs are lower. Premix molding may benefit *your* operation, too. For more information, write today to THE DOW CHEMICAL COMPANY, Midland, Michigan, Dept. 2378EX9

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# decorated dinnerware compression molded on specially designed press

Melamine dinnerware is compression molded on a Farrel Watson-Stillman press installed at Applied Plastics Division, Keystone Brass Works, Inc. The finished product, which is both handsome and durable, features molded-in flower and other decorations.

These are obtained through a critical laminating technique which actually seals the designs under the resin film. Multi-cavity molds and 24-hour, 6-day operation of the press are required to meet continuous production demands.

Since this process requires special cycling and infinite control, the press was equipped with a double-cycle control system. The tank and pumping unit were both located in a separate, adjacent room to reduce the possibility of contamination during the molding process. The press has a capacity of 500 tons with operating pressure of 2000 psi. Die-space dimensions are 36″ x 30″; stroke is 24″.

Farrel Watson-Stillman compression and transfer molding presses are available in standard designs in capacities from 50 to 1200 tons.

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